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CONTENTS.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

PAGE

I.—Contributions to Cellulose Chemistry. Acetylation of Cellulose. By C. F. Cross and E. J. Bevan 1

II.—Compounds of Phenanthraquinone with Metallic Salts. By Francis R. Japp, F.R.S., and Alfred E. Turner . . 4

III.—Action of Aldehydes and Ammonia on α-Diketones. By G. H. Wadsworth, Associate of the Normal School of Science 8

IV.—Action of Dehydrating Agents on $\alpha\omega$-Diacetylpentane. Synthesis of Methylethylhexamethylene. By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D. . 13

V.—$\alpha\omega$-Diacetyl-$\alpha\omega$-diethylpentane. By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D. 29

VI.—Frangulin. By T. E. Thorpe, F.R.S., and H. H. Robinson, M.A. 38

VII.—The Action of Chloroform and Alcoholic Potash on Hydrazines. (Part III.) By S. Ruhemann, Ph.D , M.A. . 50

VIII.—Note on the Identity of Cerebrose and Galactose. By Horace T. Brown, F.R.S., and G. Harris Morris, Ph.D., F.I.C. 57

IX.—Arabinon, the Saccharon of Arabinose. By C. O'Sullivan, F.R.S. 59

X.—The Nature of Solutions as elucidated by a Study of the Density, Electric Conductivity, Heat Capacity, Heat of Dissolution, and Expansion by Heat of Sulphuric Acid Solutions. By Spencer Umfreville Pickering, M.A. . 64

XI.—A New Method of Estimating the Oxygen dissolved in Water. By John C. Thresh, D.Sc., M.B., Medical Officer of Health 185

XII.—The Constituents of Flax. By C. F. Cross and E. J. Bevan 196

XIII.—Milk of Abnormal Quality. By Frederick James Lloyd, F.I.C. 201

XIV.—Ethyl $\alpha\alpha_1$-Diacetyladipate. By W. H. Perkin, Jun., Ph.D. 204

PAGE

XV.—$\omega\omega_1$-Diacetylbutane. By T. Rhymer Marshall, D.Sc., and W. H. Perkin, Jun., Ph.D. 241

XVI.—The Action of Chromium Oxychloride on Nitrobenzene. By G. G. Henderson, B.Sc., M.A., F.I.C., and J. Morrow Campbell, B.Sc., Donaldson Chemical Scholar, University of Glasgow 253

XVII.—Semithiocarbazides. By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Galway . . 257

XVIII.—Note on a Phenylic Salt of Phenylthiocarbamic Acid. By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Galway 268

XIX.—The Behaviour of the more Stable Oxides at High Temperatures. (Part I.) Cupric Oxide. By G. H. Bailey, D.Sc., Ph.D., and W. B. Hopkins, the Owens College . 269

XX.—The Influence of different Oxides on the Decomposition of Potassium Chlorate. By G. J. Fowler, M.Sc., and J. Grant, the Owens College 272

XXI.—Contributions to the Chemistry of Thiocarbamides. Interaction of Benzyl Chloride and Allyl Bromide, respectively, with Thiocarbamide, Monophenylthiocarbamide, and Diphenylthiocarbamide. By Emil A. Werner, Assistant Lecturer in Chemistry, Trinity College, University of Dublin 283

XXII.—Derivatives of Phenylhexamethylene. By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D. . 304

XXIII.—Some Crystallised Substances obtained from the Fruits of various species of *Citrus*. By William A. Tilden, D.Sc. Lond., F.R.S., and Charles R. Beck 323

XXIV.—Synthesis of Triazine-derivatives. By Raphael Meldola, F.R.S.. 328

XXV.—The Nature of Solutions, as Elucidated by the Freezing Points of Sulphuric Acid Solutions. By Spencer Umfreville Pickering 331

XXVI.—Contributions to the Knowledge of Mucic Acid. Part I. Hydromuconic Acid. By S. Ruhemann, Ph.D., M.A., and F. F. Blackman, B.Sc. 370

XXVII.—The Molecular Weights of Metals when in Solution. By C. T. Heycock, M.A., and F. H. Neville, M.A. . . 376

XXVIII.—The Formation of Indene-derivatives from Dibrom-α-naphthol. By Raphael Meldola, F.R.S., and Frank Hughes 393

XXIX.—The Evidence afforded by Petrographical Research of the occurrence of Chemical Change under great Pressure. By J. W. Judd, F.R.S., F.G.S., Professor of Geology in the Normal School of Science and Royal School of Mines . 404

PAGE
Annual General Meeting 426
XXX.—Researches on the Germination of some of the Gramineæ. Part I. By **Horace T. Brown**, F.R.S., and **G. Harris Morris**, Ph.D., F.I.C. 458
XXXI.—The Terminology of Hydrolysis, especially as affected by "Ferments." By **Henry E. Armstrong** 528
XXXII.—Action of Phosphoric Anhydride on Fatty Acids. Part I. By **F. Stanley Kipping**, Ph.D., D.Sc. 532
XXXIII.—Contributions from the Laboratory of Gonville and Caius College, Cambridge. No. XVIII. On the Sulphates of Antimony. By **R. H. Adie**, B.A., Scholar of Trinity College 540
XXXIV.—Phosphorous Oxide. Part I. By **T. E. Thorpe**, F.R.S., and **A. E. Tutton**, Demonstrator of Chemistry in the Normal School of Science, South Kensington . . . 545
XXXV.—An Investigation of the Conditions under which Hydrogen Peroxide is formed from Ether. By Professor **Wyndham R. Dunstan** and **T. S. Dymond** 574
XXXVI.—Note on the Preparation of Pyrocatechol. By **W. H. Perkin**, Jun., Ph.D. 587
XXXVII.—Nitrogen Trioxide and Peroxide. By **W. Ramsay**, Ph.D., F.R.S. 590
XXXVIII.—The Action of Light on Phosphorus and some of the Properties of Amorphous Phosphorus. By **Alexander Pedler**, F.I.C. 599
XXXIX.—The Action of Chlorine on Water in the Light, and the Action of Light on Certain Chlorine Acids.—By **Alexander Pedler**, F.I.C. 613
XL.—Notes on the Explosion of Sulphuretted Hydrogen and of the Vapour of Carbon Bisulphide with Air and Oxygen.—By **Alexander Pedler**, F.I.C. 625
XLI.—A Third Naphthaquinone. By **Raphael Meldola**, F.R.S., and **Frank Hughes** 631
XLII.—Diethylphosphorous Acid. By **T. E. Thorpe**, F.R.S., and **Barker North**, Associate of the Normal School of Science, South Kensington 634
XLIII.—The Relative Antiseptic Powers of Isomeric Organic Compounds. By **Thos. Carnelley**, D.Sc., Aberdeen, and **W. Frew**, F.C.S., Dundee 636
XLIV.—Contributions from the Chemical Laboratory of the University of Edinburgh. No. I. On Tertiary Butyl Mercaptan. By **Leonard Dobbin**, Ph.D. 639
XLV.—Contributions from the Chemical Laboratory of the University of Edinburgh. No. II. On Desylacetophenone. By **Alex. Smith**, B.Sc., Ph.D. 643

PAGE

XLVI.—Action of Ethyl Oxalate on Camphor. By J. Bishop Tingle, Ph.D. 652

XLVII.—On the Molecular Weights of Metals when in Solution. By C. T. Heycock, M.A., and F. H. Neville. Part II 656

XLVIII.—$\alpha\beta$-Dibenzoylcinnamene and the Constitution of Zinin's Lepiden and its Derivatives. By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D. 662

XLIX.—Crystallographical Relations of the Derivatives of Dibenzoylcinnamene. By Alfred E. Tutton, Demonstrator in Chemistry at the Normal School of Science, South Kensington 714

L.—Action of Carbon Monoxide on Nickel. By Ludwig Mond, Dr. Carl Langer, and Dr. Friedrich Quincke 749

LI.—The Milk of the Gamoose. (Preliminary Notice.) By A. Pappel and H. Droop Richmond 754

LII.—The Interaction of Iodine, Water, and Potassium Chlorate. By Henry Bassett 760

LIII.—The Action of Heat on the Chlorides and Hydroxides of Mixed Quaternary Ammonium Compounds. By N. Collie, Ph.D., and S. B. Schryver, B.Sc., the University College, London 767

LIV.—Note on a Compound from Benzoïn and Acetone. By Francis R. Japp, F.R.S., and Julius Raschen, Ph.D. . . 783

LV.—Researches on Normal and Mixed Diazoamides. By Raphael Meldola, F.R.S., and F. W. Streatfeild, F.I.C.. 785

LVI.—Note on the Action of Nitric Acid on Dibrom-α-naphthol. By Raphael Meldola, F.R.S., and Frank Hughes . . 808

LVII.—A New Method for the Estimation of Nitrates and Nitrites in Water. By R. Ormandy and J. B. Cohen, PhD., Owens College, Manchester 811

LVIII.—Action of Zinc on Dilute Sulphuric Acid. By Frank Pullinger, B.A., B.Sc., late Scholar of Corpus Christi College, Oxford 815

LIX.—A New Monobromocamphor. By J. E. Marsh . . . 828

LX.—Invertase: a Contribution to the History of an Unorganised Ferment. By C. O'Sullivan, F.R.S., and F. W. Tompson 834

LXI.—Contributions to the Knowledge of Mucic Acid. Part II. Action of Phosphorus Pentachloride on Mucic Acid. By S. Ruhemann, Ph.D., M.A., and W. J. Elliott, B.A. . . 931

LXII.—Contributions to the Knowledge of Mucic Acid. Part III. Hydromuconic Acid. By S. Ruhemann, Ph.D., M.A. 937

PAGE
LXIII.—Diphenylfurfuran. By W. H. PERKIN, Jun., Ph.D., F.R.S., and A. SCHLOESSER, Ph.D., M.Sc. 944
LXIV.—Note on the Reduction of Aromatic Amides. By A. HUTCHINSON, B.A., Scholar of Christ's College, Cambridge . 957
LXV.—Some Improved Vacuum Joints and Taps. By W. A. SHENSTONE 958
LXVI.—The Production of Camphor from Turpentine. By J. E. MARSH, B.A., and R. STOCKDALE, B.A. 961
LXVII.—*p*-Desylphenol. By FRANCIS R. JAPP, F.R.S., and G. H. WADSWORTH, Associate of the Normal School of Science 965
LXVIII.—Paraxylenesulphonic Acids. By GERALD T. MOODY, D.Sc., Demonstrator in the Chemical Department, City and Guilds of London Institute, Central Institution, and T. G. NICHOLSON 974
LXIX.—Action of Phosphoric Anhydride on Fatty Acids. Part II. By F. STANLEY KIPPING, Ph.D., D.Sc. . . . 980
LXX.—An Investigation of the Conditions under which Hydrogen Peroxide is formed from Ether. (Second Notice.) By WYNDHAM R. DUNSTAN and T. S. DYMOND 988
LXXI.—Contributions from the Laboratories of the Heriot Watt College, Edinburgh. On Berberine. Part II. By W. H. PERKIN, Jun., Ph.D., F.R.S. 991

University of [illegible]

JOURNAL

OF

THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*Contributions to Cellulose Chemistry.*

By C. F. **Cross** and E. J. **Bevan**.

Acetylation of Cellulose.

In the course of our investigations of the constitution of the lignocelluloses (Trans., 1889, **55**, 199), we have had occasion to study the action of acetic anhydride on jute; at the boiling point, this is partially dissolved by the anhydride, and on pouring the solution into water a flocculent precipitate of an acetyl derivative is obtained; the increase in weight was found to be from 12 to 13 per cent. If sodium acetate is added to the anhydride (Liebermann's method), the yield is increased to 120 per cent., and still better results are obtained by the use of a trace of zinc chloride.

The last method, which is due to Franchimont (*Ber.*, **12**, 2059), has been frequently employed of late, notably for the preparation of the higher acetyl derivatives of the soluble carbohydrates (*Ber.*, **12**, 1264 and 2207), and, before proceeding with our research, we thought it better to familiarise ourselves with the method by studying the action of acetic anhydride upon cellulose itself.

It is well known that cellulose does not react with acetic anhydride even in the presence of sodium acetate, unless the temperature be raised to 180°. Franchimont, however, has found (*loc. cit.*) that in presence of zinc chloride, cellulose is rapidly attacked at the boiling point of the anhydride, the chief product being the triacetate previously described by Schutzenberger (*Compt. rend.*, **68**, 814), a true cellulose derivative; whereas when sulphuric acid is employed as the auxiliary, the molecule is resolved into a complex of crystalline derivatives of lower molecular weight.

In our experiments, purified cotton was boiled for 16 hours with acetic anhydride containing in solution a trace of zinc chloride, when it was found that the whole of the fibre had disappeared. On pouring the solution into water, a copious precipitate was obtained, which, after washing and drying, was found on combustion to contain 52·3 per cent. of carbon and 5·6 per cent. of hydrogen; on hydrolysis, it afforded a quantity of acetic acid equal to 80 per cent. of the substance.

We purified a portion by dissolving it in acetic acid and treating it with potassium permanganate. The acetyl-compound is not acted on, whereas the traces of other compounds, chiefly aldehydic, which accompany it, and which we may mention, give to the solution an orange-green fluorescence, are easily oxidised and removed. The yield of the purified product amounted in several preparations to 170—190 per cent. of the original cotton fibre. On combustion, it gave the following numbers:—

0·1007 gave 0·1912 CO_2 and 0·0537 H_2O = carbon 51·6 and hydrogen 5·9.

These numbers, together with the yield and the amount of acetic acid obtained on hydrolysis, pointed clearly to the fact that we had obtained a higher derivative than the triacetate. The hydrolysis numbers are the most trustworthy as an indication of the composition of such compounds, as the difference in the yield of acetic acid between the tri- (62·5), tetra- (72·7), and penta-derivatives (80·7 per cent.) are considerable, whereas the percentages of carbon and hydrogen vary but slightly. The hydrolysis number obtained by us for the purified compound was equal to 81 per cent. of acetic acid. This will be seen to be in close accord with the number calculated for the pentacetate, namely, 80·7. From this fact alone, therefore, there can be no doubt that the compound we have obtained is the pentacetate.

It dissolves freely in acetic acid, and it is precipitated from this solution on the addition of water in dense, opaque masses, which dry to a granular powder. It melts at a high temperature to a clear liquid, without decomposition. It is soluble in boiling nitrobenzene, and the solution gelatinises on cooling. This property is regarded by Franchimont (*Rec. Trav. Chim.*, **2**, 241) as characteristic of the ethereal salts of cellulose, in contradistiuction to those of allied carbohydrates of lower molecular weight.

Sulphuric acid dissolves it, but at the same time decomposes it, although from its solution in a nitrating mixture of equal volumes of sulphuric acid and nitric acid it is precipitated apparently unchanged. On this point we may cite the following numbers:—0·120 gram dissolved yielded 0·119 gram on reprecipitation. The precipitate, when examined for nitrogen by Eder's method (*Ber.*, **13**, 169), gave no nitric oxide, neither did it yield any sulphuric acid when fused with potassium hydrate and nitrate. Nitric acid also dissolves the pentacetyl-compound, and it is reprecipitated by water without change. It resists prolonged boiling with dilute mineral acid. As stated before, it is not oxidised by permanganate, and the products of alkaline hydrolysis do not reduce Fehling's solution. It gives no colour with iodine solution, even with the addition of sulphuric acid. When hydrolised with solution of soda, it yields a residue of cellulose which amounts to 32 per cent. of the original weight. The calculated number is 43 per cent., but the difference may be accounted for by the fact that the cellulose as it is formed is itself hydrolysed.

In endeavouring to arrive at the constitution of cellulose, we have hitherto been hampered by the limited number of true derivatives obtainable. Conclusions drawn from the composition of the nitrates as to the number of OH groups in the molecule are to some extent deceptive, and for the following reasons:—

1. The mode of their formation and the nature of the $-O{\cdot}NO_2$ groups preclude us from assuming that the substitution of hydroxyl is at a maximum in the case of the highest nitrate.

2. The products of alkaline hydrolysis are not simple; the presence of aldehydic compounds and oxalic acid, and the formation of nitrite are evidences of a fundamental resolution of the cellulose molecule. The acetates, on the other hand, being formed in a less drastic manner, enable us to arrive at the probable constitution of cellulose with a greater degree of probability.

The triacetate recognised hitherto as the highest derivative appeared to confirm the inference from the study of the nitrate, namely, that the unit group, $C_6H_{10}O_5$, contains three OH groups. The latest discussion on this subject is that of Franchimont, in a paper on "The Oxycellulose of Witz" (*Rec. Trav. Chim.*, **2**, 241). Reviewing all the evidence, including his own observation that cellulose is quantitatively converted into glucose, he concludes that cellulose is the condensed representative of *n* glucose-groups united by "bonds of dehydration," expressed in the aggregate by the equation, $nC_6H_{12}O_6 - (n-1)H_2O$.

On the other hand, the conclusion to which the results of our investigation leads is that cellulose contains neither aldehydic nor ketonic oxygen; in support of this we may cite a prominent fact of modern cellulose technology. Cellulose is completely isolated from the lignose with which it is associated in wood by the powerfully hydrolytic action of sulphurous acid, with or without the addition of an earthy base. This harmonises entirely with what we know of the constitution of the lignose molecule, viz., that it is a condensed aldehyde and ketone. It is a reasonable inference from this that the C_6-groups of cellulose are not united by aldehydic condensation, for, whilst such a condensation might resist alkaline hydrolysis, as Franchimont points out, it would need to differ from all known types of condensation of ketones or aldehydes to withstand acid hydrolysis.

The alternative view which we have to consider is a C_6-nucleus combined with 5 OH-groups and 5 or 6 H-atoms—as our analytical results accord equally well or rather better, with the latter number. Further as we have no evidence of the presence of C : C groups, we should be necessarily involved, on this view, in the assumption of a closed chain of carbon-atoms, if not in cellulose itself, at least in the pentacetyl derivatives.

We do not desire to attach too much importance to our own conclusions: but they will be useful as a working hypothesis in carrying on the investigation which the present results indicate.

The old views as to the constitution of cellulose need revising in the light of recent research. The establishment of a C_5-formula for such carbohydrates as arabinose and xylose; a closed ring formula for inosite; and the numerous transitions from closed to open carbon rings and *vice versa*, which the researches of Hantzsch and Zincke have brought to light, should lead chemists to reconsider the constitution of cellulose.

The results detailed in the present paper at least afford a new point of view from which to regard the problem.

We published a preliminary note in the "Chemical News," on this research, explaining how we had come to reopen a subject left unfinished some years ago by Professor Franchimont. We have received a letter from him expressing his satisfaction that other chemists had taken in hand an investigation which he had been obliged to abandon.

II.—*Compounds of Phenanthraquinone with Metallic Salts.*

By Francis R. Japp, F.R.S., and Alfred E. Turner.

In the course of an investigation of the condensations of phenanthraquinone with other organic compounds, a solution of zinc chloride in acetic acid was employed as a condensing agent. It was observed that the phenanthraquinone was precipitated from the accetic acid solution in the form of dark reddish-brown needles, which proved to contain zinc chloride. We therefore examined the behaviour of various quinones and other diketones towards metallic salts and found that, in certain cases, by employing the proper solvent, molecular compounds could be obtained. The following have been analysed:—

(1.) An equimolecular compound of phenanthraquinone with zinc chloride: $C_{14}H_8O_2,ZnCl_2$.

(2.) A compound of 2 mols. of phenanthraquinone with 1 mol. of mercuric chloride: $(C_{14}H_8O_2)_2,HgCl_2$.

(3.) A corresponding compound with mercuric cyanide:

$$(C_{14}H_8O_2)_2,HgCy_2.$$

The difference in the combining value of the mercury and zinc salts is worthy of note.

No compounds could be obtained with benzoquinone, α-naphthaquinone, anthraquinone, diacetyl, or benzil; but β-naphthaquinone gave a compound (not analysed) with mercuric chloride, closely resembling in appearance the corresponding compound from phenanthraquinone.

No compounds with oxy-salts could be obtained.

If it is permissible to generalise from so few cases, it would appear that in order that a dicarbonyl-compound may combine with metallic salts, its two carbonyl-groups (1) must be directly united and (2) must form part of a closed chain, that is, must be in the quinone condition. No such compounds are formed with para-quinones or with open-chain α-diketones.

The above molecular compounds are intensely coloured, showing that the quinone retains in them its distinctive character. They are in this respect sharply distinguished from the colourless compounds of the orthoquinones with hydrogen sodium sulphite, the formation of which involves a reduction and which are to be regarded as quinol derivatives: phenanthraquinone hydrogen sodium sulphite being $C_{14}H_8(OH)(OSO_3Na)$.

Phenanthraquinone Zinc Chloride, $C_{14}H_8O_2,ZnCl_2$.—To prepare this compound, a hot, strong solution of zinc chloride in glacial acetic acid is added in excess to a hot solution of phenanthraquinone in the same solvent. The molecular compound separates almost instantly. As it is decomposed by the moisture of the air it is best filtered, with the aid of the filter-pump, through a funnel consisting of a wide glass tube drawn out to a narrow neck, plugged with cotton wool, and connected at the top with a drying tube. The compound is washed on the funnel with boiling glacial acetic acid, in which it is only very sparingly soluble, quickly transferred to a weighing bottle, and dried at 130° until the weight is constant.

Even when the liquid containing the crystals is allowed to cool before filtering, there is no danger of the excess of zinc chloride crystallising out. On the other hand, the washing with hot glacial acetic acid is absolutely necessary to remove *adhering* zinc chloride.

The analysis was conducted by decomposing a weighed quantity of the substance by boiling it with water, allowing the liquid with the precipitate to stand overnight, collecting the phenanthraquinone on a weighed filter, washing with cold water to which two or three drops of hydrochloric acid had been added, and drying at 100° before weighing.

	Substance.	Phenanthraquinone.
I	1·101	0·663
II	1·117	0·676

	Calculated for $C_{14}H_8O_2,ZnCl_2$	Found. I.	Found. II.
$C_{14}H_8O_2$ in 100 parts	60·46	60·21	60·51

Different preparations were analysed.

The compound forms dark reddish-brown needles which may be heated above 300° without melting. Both water and alcohol decompose it. When exposed to the air at ordinary temperatures, it attracts moisture, its colour changing to the orange-yellow of phenanthraquinone. A very small quantity of water in the acetic acid used in the preparation of the compound prevents its formation altogether.

Phenanthraquinone Mercuric Chloride $(C_{14}H_8O_2)_2,HgCl_2$. — Some difficulty was experienced in finding a solvent from which this compound would crystallise in a pure state. In alcoholic solution it is not formed at all; glacial acetic deposits mainly phenanthraquinone, with mere traces of the new compound; chloroform deposits the molecular compound as a brilliant scarlet powder, contaminated, however, with free mercuric chloride, which is very sparingly soluble in chloroform. Acetone was found to give the best results.

When hot concentrated solutions of mercuric chloride and phenanthraquinone in acetone are mixed, the liquid, on cooling, deposits crystals of the double compound, but phenanthraquinone is apt to separate out at the same time. This is avoided, however, by the following method: To a boiling strong solution of mercuric chloride in acetone, finely divided phenanthraquinone is added and the boiling is continued. The double compound separates almost immediately as a heavy scarlet powder. The hot supernatant liquid is poured off from the powder, and the latter is dissolved in boiling acetone. On cooling, this second solution deposits the double compound in red, obliquely truncated prisms, which, after washing with acetone and drying at 100°, are pure for analysis. They melt at 222—223°.

As it was feared that boiling with water would not extract the whole of the mercuric chloride, a weighed quantity of the crystals was dissolved in boiling alcohol, which decomposes them; the phenanthraquinone was precipitated by the addition of an excess of water; the alcohol was boiled off, afterwards allowing the liquid with the precipitate to stand overnight: and finally the phenanthraquinone was collected as before on a weighed filter. The filtrate in this process was always tinged yellow, owing to the presence of traces of unprecipitated phenanthraquinone, which accounts for the slight deficit in the analyses.

	Substance.	Phenanthraquinone.
I	1·842	1·101
II	1·131	0·682
III	1·077	0·647

	Calculated for $(C_{14}H_8O_2)_2,HgCl_2$.	Found. I.	II.	III.
$C_{14}H_8O_2$ in 100 parts..	60·55	59·77	60·30	60·08

In the foregoing analyses, different preparations were employed.

Phenanthraquinone Mercuric Cyanide $(C_{14}H_8O_2)_2HgCy_2$.—Hot saturated solutions of phenanthraquinone and mercuric cyanide in acetone were mixed and allowed to cool slowly. Well-shaped red crystals were deposited, which showed on certain faces a greenish reflex, visible only when the crystals were under the mother-liquor. The melting-point was 222—223°, the same as that observed in the mercuric chloride compound. The method of analysis was identical with that employed in the case of the mercuric chloride compound, and the percentage of phenanthraquinone found was, for the reason already assigned, somewhat low.

	Substance.	Phenanthraquinone.
I............	1·122	0·691
II............	1·638	1·044
III............	1·288	0·794

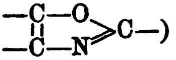
	Calculated for $(C_{14}H_8O_2)_2,HgCy_2$.	Found. I.	II.	III.
Phenanthraquinone in 100 parts	62·28	61·58	61·85	61·65

Different preparations were analysed.

Normal School of Science,
South Kensington.

III.—*Action of Aldehydes and Ammonia on α-Diketones.*

By G. H. Wadsworth, Associate of the Normal School of Science.

The condensations of α-diketones with aldehydes and ammonia have hitherto been studied chiefly in the case of phenanthraquinone and benzil. The reaction has been shown to vary both with the diketone and with the aldehyde employed. The most frequently occurring reaction of this class is that in which glyoxalines are formed: as, for example, by the action of fatty aldehydes, and also of certain aldehydes of the benzene series, on benzil. Of less frequent occurrence is the formation of oxazoles (*i.e.*, compounds containing the complex  $\begin{array}{l}-\mathrm{C}-\mathrm{O}\\ \;\;\parallel\\ -\mathrm{C}-\mathrm{N}\end{array}\!\!>\mathrm{C}-$): this reaction is exemplified in the condensations of phenanthraquinone with several of the benzenoid aldehydes. Other reactions, such as those which yield the complex compounds obtained from benzil with salicylaldehyde and cinnamaldehyde respectively, occur only in isolated cases.*

It appeared of interest to ascertain what the action would be in the case of some typical α-diketone of the fatty series, such as diacetyl. With the kind consent of Dr. von Pechmann, by whom diacetyl was first described, and by whose method the material employed in this investigation was prepared, I have, therefore, studied its reactions with aldehydes and ammonia.

The aldehydes employed were benzaldehyde, salicylaldehyde, and cinnamaldehyde; but in each case nothing but a glyoxaline was formed, and none of the abnormal reactions which occur in the case of benzil were observed.

I have also studied the action of fatty aldehydes and ammonia on phenanthraquinone, but failed to obtain condensation-compounds. A benzene-fatty aldehyde, however—cinnamaldehyde—gave an oxazole with phenanthraquinone and ammonia.

Benzaldehyde, Diacetyl, and Ammonia.—10 grams of diacetyl, with the molecular proportion of benzaldehyde, were dissolved in a small quantity of alcohol, and heated with an excess of alcoholic ammonia for half an hour on the water-bath. The new compound was precipitated by the addition of water, redissolved in dilute hydrochloric acid, the base reprecipitated from the filtered solution by ammonia, and purified by repeated recrystallisation from hot benzene.

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* Japp and Streatfeild, Trans., 1882, 155; Japp and Hooker, Trans., 1884, 673; Japp and Wynne, Trans., 1886, 464. A fairly complete summary of the results obtained in this field is given in the new *Watts's Dictionary of Chemistry*, vol. i, p. 465.

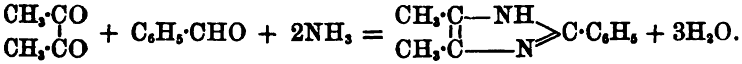
Analysis of the substance, dried at 100°, gave figures agreeing with the formula $C_{11}H_{12}N_2$:—

	Substance.	CO_2.	H_2O.
I........	0·1525	0·4284	0·0977
II........	0·1456	0·4089	0·0938

	Substance.		v	t.	p.
III....	0·0832	Dry N + NO	22·32 c.c.	20°	411 mm.
		„ N......	22·32 „	20	378 „
IV....	0·0827	Dry N + NO	22·32 c.c.	24	416 mm
		„ N......	22·32 „	24	373 „

	Calculated for $C_{11}H_{12}N_2$.		Found.			
			I.	II.	III.	IV.
C_{11}........	132	76·74	76·60	76·58	—	—
H_{12}.......	12	6·97	7·12	7·15	—	—
N_2........	28	16·27	—	—	16·30	16·16
	172	99·98				

The compound is formed according to the equation—



$$\begin{array}{l}CH_3\cdot CO\\ \;\;\;|\\ CH_3\cdot CO\end{array} + C_6H_5\cdot CHO + 2NH_3 = \begin{array}{l}CH_3\cdot C—NH\\ \;\;\;\;\;\;\;\;\Vert\\ CH_3\cdot C——N\end{array}\!\!>C\cdot C_6H_5 + 3H_2O.$$

and would be *phenyldimethylglyoxaline.*

Phenyldimethylglyoxaline crystallises from benzene in slender needles containing benzene of crystallisation, which is given off on exposure to air. It is readily soluble in alcohol. It melts at 230—234°, and at a higher temperature volatilises, condensing in needles, which showed the same melting point.

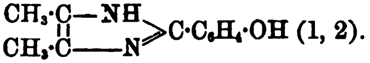
0·6720 gram of the substance, crystallised from benzene and dried by brief exposure to air, lost, on heating at 100°, 0·1294 gram benzene, equal to a loss of 19·26 per cent. The formula $(C_{11}H_{12}N_2)_2,C_6H_6$ requires a loss of 18·48 per cent.

The platinichloride is precipitated on the addition of platinic chloride to a solution of the base in hydrochloric acid. It forms yellow needles and is anhydrous.

0·1380 gram of the salt, previously dried at 100°, gave on ignition 0·0356 gram of platinum.

	Calculated for $(C_{11}H_{12}N_2,HCl)_2PtCl_4$.	Found.
Pt in 100 parts........	25·82	25·79

Salicylaldehyde, Diacetyl, and Ammonia.—The operation was conducted like the foregoing, employing 10 grams of diacetyl and the molecular proportion of salicylaldehyde; and the resulting compound was purified by recrystallisation from dilute alcohol. Analysis gave numbers agreeing with the formula of *orthohydroxyphenyldimethylglyoxaline*.



$$\left.\begin{array}{l} CH_3\cdot C-NH \\ \quad\ \| \\ CH_3\cdot C-\!\!-N \end{array}\right\rangle C\cdot C_6H_4\cdot OH\ (1,\ 2).$$

	Substance.	CO_2.	H_2O.
I........	0·2100	0 5395	0·1213
II........	0·1475	0·3790	0·0864

	Substance.		*v*.	*t*.	*p*.
III....	0·0856	Dry N + NO	22·32 c.c.	29°	396 mm.
		„ N......	22·32 „	29	375 „

	Calculated for $C_{11}H_{12}N_2O$.		Found.		
			I.	II.	III.
C_{11}........	132	70·21	70·06	70·07	—
H_{12}.......	12	6·38	6·41	6·50	—
N_2........	28	14·89	—	—	15·02
O	16	8·51	—	—	—
	188	99·99			

The compound crystallises from dilute alcohol in colourless, satiny needles melting at 218°, and from benzene in star-shaped forms. The alcoholic solution shows a blue fluorescence.

The hydrochloride is very sparingly soluble in cold water. From its solution the platinichloride is precipitated in yellow needles of the formula $(C_{11}H_{12}N_2O,HCl)_2PtCl_4,2H_2O$ on the addition of platinic chloride, but owing to the sparing solubility of the hydrochloride, is apt to be contaminated with the latter salt, for which reason the percentage of platinum was found too low.

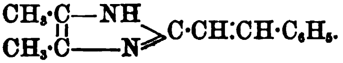
0·3358 gram of the air-dried platinum salt lost on heating at 100° 0·0150 gram, and the remaining 0·3208 gram gave on ignition 0·0772 gram platinum.

	Calculated for $(C_{11}H_{12}N_2O,HCl)_2PtCl_4,2H_2O$.	Found.
H_2O in 100 parts............	4·38	4·46

	Calculated for $(C_{11}H_{12}N_2O,HCl)_2PtCl_4$.	Found.
Pt in 100 parts..............	24 74	24·06

Cinnamaldehyde, Diacetyl, and Ammonia.—10 grams of diacetyl with the molecular proportion of cinnamaldehyde were heated with alcoholic ammonia in a sealed tube at 100° for about an hour. The contents of the tube, after expelling the alcohol by evaporation, were acidified with strong hydrochloric acid and diluted with 3 to 4 times their bulk of water; this precipitated most of the resin, which is formed in large quantity in this reaction. The resin was filtered off as quickly as possible, after which the hydrochloride of the new base began to separate from the filtrate in the form of yellowish needles, the separation being facilitated by the addition of a large excess of fuming hydrochloric acid to the solution. This salt was freed from adhering resin by washing with ether, then dissolving in a small quantity of alcohol and reprecipitating with ether, by which means it was obtained colourless. From a hot aqueous solution of the hydrochloride, ammonia precipitated the base, which was then purified by recrystallisation from benzene. It formed colourless, warty crystals melting at 201—202°, very soluble in alcohol and in ether, sparingly soluble in petroleum, very slightly soluble in boiling water.

A nitrogen determination showed that in this case also a glyoxaline *cinnamenyldimethylglyoxaline*—



had been formed.

Substance.		v.	t.	p.
0·0878	Dry N + NO ..	13·5 c.c.	19°	597 mm.
	„ N	13·5 „	19	582 „

	Calculated for $C_{13}H_{14}N_2$.	Found.
N in 100 parts	14·00	14·14

On the addition of platinic chloride to a solution of the hydrochloride, the platinichloride is precipitated in the form of microscopic yellow needles, which are anhydrous.

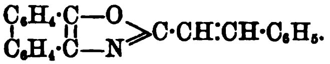
0·1624 gram of the salt, which did not lose weight at 120°, gave on ignition 0·0394 gram platinum.

	Calculated for $(C_{13}H_{14}N_2,HCl)_2PtCl_4$.	Found.
Pt in 100 parts........	24·22	24·15

Cinnamaldehyde, Phenanthraquinone, and Ammonia.—10 grams of phenanthraquinone with the molecular proportion of cinnamaldehyde were heated with an excess of alcoholic ammonia in a sealed tube at

100°. On cooling, a substance was deposited in a solid state; this was separated by filtration and dissolved in hot glacial acetic acid, from which it crystallised in slender, yellow needles: these, after recrystallising twice from the same solvent, melted constantly at 171—172°. The compound is also readily soluble in benzene and in carbon bisulphide. It does not form salts with acids.

The results of analysis pointed to the formula $C_{23}H_{15}NO$, which is that of a *cinnamenyldiphenyleneoxazole*.



$$\begin{array}{l} C_6H_4\cdot C{-}O \\ \,\mid \qquad\;\; \| \\ C_6H_4\cdot C{-}N \end{array}\!\!>C\cdot CH{:}CH\cdot C_6H_5.$$

	Substance.	CO_2.	H_2O.
I	0·1220	0·3844	0·0532

	Substance.		v.	t.	p.
II	0·1259	N + NO..	9·02 c.c.	20°	408 mm.
		N	9·02 „	20	405 „

	Calculated for $C_{23}H_{15}NO$.		Found. I.	Found. II.
C_{23}	276	85·98	85·92	—
H_{15}	15	4·67	4·84	—
N	14	4·36	—	4·48
O	16	4·98	—	—
	321	99·99		

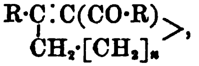
Normal School of Science,
South Kensington.

IV.—*Action of Dehydrating Agents on αω-Diacetylpentane. Synthesis of Methylethylhexamethylene.*

By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D.

In a paper which we had the honour of communicating to the Society some time ago, we described the preparation and properties of αω-diacetylpentane and of αω-dibenzoylpentane, and stated also that our object in preparing these diketones was to study their behaviour with dehydrating and reducing agents.

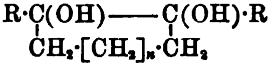
It was thought possible that diketones of the constitution $R\cdot CO\cdot CH_2\cdot[CH_2]_n\cdot CH_2\cdot CO\cdot R$ might, under the influence of dehydrating agents, undergo internal condensation, and be converted into compounds having the constitution



$$\left.\begin{array}{l}R\cdot C{:}C(CO\cdot R)\\ \ \ \vert\\ CH_2\cdot[CH_2]_n\end{array}\right>,$$

a reaction which, to some extent, would be analogous to the formation of mesityl oxide from acetone.

The study of the action of reducing agents on diacetyl- and dibenzoyl-pentane also possessed great interest, as it was considered probable that in this manner dihydroxy-derivatives of the constitution



$$\begin{array}{l}R\cdot C(OH)\text{——}C(OH)\cdot R\\ \ \ \ \ \vert\qquad\qquad\quad\ \vert\\ \ \ \ CH_2\cdot[CH_2]_n\cdot CH_2\end{array}$$

would be obtained. Both these reactions would, naturally, be controlled by the value of *n*.

Our views regarding the probable course of these reactions have been confirmed experimentally, and in the present paper we beg to lay before the Society the results which we have obtained in studying the action of dehydrating agents on diacetylpentane.

When diacetylpentane is treated with concentrated sulphuric acid, it is converted into a colourless liquid of the composition $C_9H_{14}O$.

$$C_9H_{16}O_2 - H_2O = C_9H_{14}O.$$

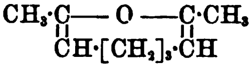
Considerable difficulty has been experienced in determining the constitution of this interesting substance, as, in accordance with the present views on the structure of organic compounds, a substance derived from diacetylpentane by the elimination of one molecule of water might be represented by any one of the following constitutional formulæ:—

I. $CH_3{\cdot}C{:}C{\cdot}[CH_2]_4{\cdot}CO{\cdot}CH_3$

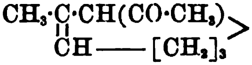
II. $CH{:}C{\cdot}[CH_2]_5{\cdot}CO{\cdot}CH_3$

III. $CH_2{:}C{:}CH{\cdot}[CH_2]_4{\cdot}CO{\cdot}CH_3$

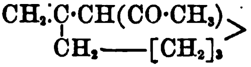
IV.



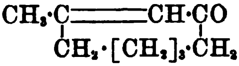
V.



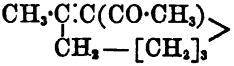
VI.



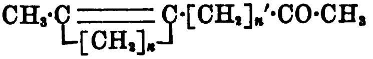
VII.



VIII.



IX.



$\left(\begin{array}{l} n = 1, 2, \text{ or } 3 \\ n' = 3, 2, \text{ or } 1 \end{array}\right)$

The results of experiments which bear directly on the question of the constitution of this compound $C_9H_{14}O$, briefly stated, are the following:—

It undergoes no change when treated with 80 per cent. sulphuric acid, or when heated with a concentrated solution of mercuric chloride.

It is not acted on by phosphoric anhydride in ethereal solution.

It combines readily with hydroxylamine, yielding an oxime, $C_9H_{15}NO$, and with phenylhydrazine, forming a hydrazone, $C_{15}H_{20}N_2$.

When treated with sodium in moist ethereal solution, it combines directly with 4 atoms of hydrogen, and is converted into an alcohol, $C_9H_{18}O$.

The iodide from this alcohol is reduced when it is heated with fuming hydriodic acid and amorphous phosphorus, yielding a hydrocarbon, C_9H_{18}.

αω-Diacetyl-*αω*-diethylpentane, $COMe{\cdot}CHEt{\cdot}[CH_2]_3{\cdot}CHEt{\cdot}COMe$, is not acted on by cold concentrated sulphuric acid.

αω-Dibenzoylpentane, $COPh{\cdot}[CH_2]_5{\cdot}COPh$, when warmed with phosphoric anhydride, is converted into a compound of the composition $C_{19}H_{18}O$.

From these facts, the constitution of the compound $C_9H_{14}O$ may be argued with a considerable degree of certainty. Its negative behaviour with 80 per cent. sulphuric acid and with mercuric chloride is strong evidence against the constitution I or II, because substances of this nature (derivatives of acetylene), under the same conditions as those employed, almost invariably combine with 1 mol. of water, and are converted into saturated compounds.

The fact that the compound $C_9H_{14}O$ is not acted on by phosphoric anhydride goes to show that the first three formulæ are all improbable, as a compound possessing the constitution I, II, or III would probably be converted into an unsaturated hydrocarbon C_9H_{12}.

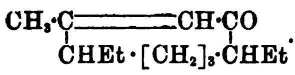
The formation of the oxime and the hydrazone shows that it is a ketone, and cannot have the constitution represented by formula IV, A conclusive proof of the inadmissibility of the formulæ I, II, III, and IV is afforded by the behaviour of the compound $C_9H_{14}O$ on reduction; when treated with sodium in moist ethereal solution, and subsequently with fuming hydriodic acid, it is converted into a hydrocarbon C_9H_{18}, whereas a substance represented by any one of these four formulæ would yield a normal paraffin C_9H_{20}.

It is, therefore, an easy task to prove conclusively that the constitution of the compound $C_9H_{14}O$ is not represented by any of the first four formulæ, but it is much more difficult to distinguish between the remaining five.

A compound having the constitution shown in V, VI, VII, VIII, or IX would be expected to behave in most respects like the substance $C_9H_{14}O$, that is, to give an oxime and a hydrazone, to yield an alcohol $C_9H_{16}O$ on reduction, and when heated with hydriodic acid to be converted into a hydrocarbon C_9H_{18}.

The behaviour of αω-diacetyl-αω-diethylpentane with sulphuric acid affords, however, a means of deciding between these formulæ. An examination of the formulæ V to IX shows clearly that the presence of a methylene-group in direct combination with the carbonyl-group is necessary to the formation of the compound $C_9H_{14}O$, only if it possesses the constitution shown in VIII; if, on the other hand, it had the constitution V, VI, VII, or IX, its formation could take place if one of the hydrogen-atoms in both these methylene-groups were replaced by a radicle such as ethyl, or in other words, diacetyldiethylpentane, $COMe\cdot CHEt\cdot[CH_2]_3\cdot CHEt\cdot COMe$, should give a condensation-product when treated with sulphuric acid just as readily as diacetylpentane.

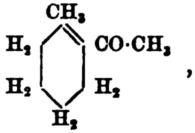
Supposing, for example, that the formula VII represents the constitution of the compound $C_9H_{14}O$, diacetyldiethylpentane should yield an analogous condensation-product of the constitution



$$\begin{array}{l} CH_3\cdot C \!=\!=\!=\!=\! CH\cdot CO \\ \quad | \qquad\qquad\qquad | \\ \; CHEt\cdot[CH_2]_3\cdot CHEt \end{array}.$$

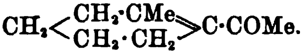
If, however, the formula VIII represents its constitution, it is obvious that no analogous reaction could take place in the case of diacetyldiethylpentane.

The results of two separate experiments have shown that diacetyldiethylpentane does not undergo internal condensation when subjected to the action of sulphuric acid under exactly the same conditions as those employed in the preparation of the compound $C_9H_{14}O$, and that not a trace of a compound corresponding with this anhydro-derivative is formed.

This behaviour can only be explained by assuming that the constitution of the compound $C_9H_{14}O$ is represented by formula VIII, and that it is Δ^1-orthomethylacetyltetrahydrobenzene,*  , (Δ^1-orthomethyltetrahydrobenzene methyl ketone).

Dibenzoylpentane, $COPh\cdot[CH_2]_5\cdot COPh$, when warmed with phosphoric anhydride, is readily converted into a compound $C_{19}H_{18}O$; if, as is probable, this compound should, on further investigation, prove to have a constitution analogous to that of the condensation-product of diacetylpentane, this fact would be additional evidence in favour of our views regarding the mechanism of these internal condensations by proving the inadmissibility of the formulæ II, III, VI, and VII. As we are at present engaged in examining this compound, and in investigating the behaviour of dibenzoylpentane with reducing agents, we hope to be able to communicate the results to the Society at an early date.

Orthomethyltetrahydrobenzene Methyl Ketone,



$$CH_2{<}\begin{matrix}CH_2\cdot CMe\\ CH_2\cdot CH_2\end{matrix}{\geqslant}C\cdot COMe.$$

Orthomethyltetrahydrobenzene methyl ketone (orthomethylacetyltetrahydrobenzene) is formed by the action of dehydrating agents on *aω*-diacetylpentane; it is best prepared by dissolving the diketone in concentrated sulphuric acid.

Diacetylpentane (not more than 30 grams) is added in small portions at a time to six or eight times its volume of concentrated sulphuric acid; as considerable evolution of heat occurs, the solution is cooled under the tap after each addition of the diketone, otherwise the yield is decreased. The resulting solution, which varies in colour from brownish-red to dark brown, is kept in a loosely-stoppered flask at the ordinary temperature from one to two days, during which time it darkens in colour, and a slight evolution of sulphurous anhydride occurs. The solution is then poured into a large volume of cold water, the greenish-yellow oil which is precipitated is extracted by shaking two or three times with ether, and the ethereal extract, after having been dried over potassium carbonate, is evaporated. A yellow, mobile oil, smelling strongly of peppermint, is obtained; the yield of the crude product is, on the average, 85—90 per cent. of the diketone employed. When this oil is distilled under the ordinary pressure, a small quantity passes over between 120° and 190°, but the principal portion distils between 190° and 210°; if the distillation is discontinued as soon as the thermometer rises above 210—215°, a small quantity of a thick, brown oil, which will be referred to below, remains in the flask.

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* Compare Baeyer. "Ueber die Constitution des Benzols" (*Annalen*, **245**, 111).

The fraction 190—210° still contains traces of unchanged diketone; pure orthomethyltetrahydrobenzene methyl ketone, boiling constantly at 205—206°, can only be obtained by again treating this product with sulphuric acid and fractionating two or three times under the ordinary pressure. The analysis gave the following results:—

0·1855 gram of substance gave 0·5294 gram CO_2 and 0·1720 gram H_2O.

	Calculated for $C_9H_{14}O$.	Found.
C........	78·26 per cent.	77·84 per cent.
H........	10·14 „	10·30 „
O........	11·60 „	11·86 „

Orthomethyltetrahydrobenzene methyl ketone is a colourless, mobile oil with a strong odour of peppermint, and a sharp, somewhat bitter taste. It boils at 205—206° (about 755 mm.) without decomposition, and is readily volatile with steam. It is insoluble in and specifically lighter than water, but it is miscible with the ordinary organic solvents in all proportions. It does not combine with sodium hydrogen sulphite even when kept for a long time with a saturated aqueous solution of the salt, but it combines readily with hydroxylamine. When treated with excess of sodium in moist ethereal solution, it is converted into orthomethylhexamethylene methyl carbinol.

In order to determine the constitution of this compound, $C_9H_{14}O$, it was necessary, in the first place, to ascertain whether it contained a "treble linking;" the following experiments were made with this object:—

A small quantity of the pure compound was dissolved in 80 per cent. sulphuric acid, and the solution kept for a few days at the ordinary temperature; it was then diluted with water, warmed for about half an hour on the water-bath, and after adding a large volume of water, extracted with ether. The boiling point and other properties of the oil which was obtained showed that it consisted entirely of the original substance, no reaction having taken place.

About 4 grams of the pure compound was mixed with a warm, concentrated, aqueous solution of mercuric chloride, and the mixture heated at 95—98° for three hours with constant shaking. A small quantity of the mercuric salt seemed to be reduced, but otherwise no reaction was observed. The mixture was then warmed with a little concentrated hydrochloric acid, the oil extracted with ether, and distilled. The whole passed over within a range of a few degrees, and consisted of the original substance.

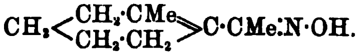
These experiments having shown that the compound $C_9H_{14}O$ does not combine with 1 mol. of water when submitted to the treatment usually employed in the case of substances containing trebly-bound carbon-atoms, it seemed interesting to ascertain, whether, under the influence of dehydrating agents more powerful than concentrated sulphuric acid, it would be converted into a hydrocarbon C_9H_{12}. The formation of such a compound would have shown that the original oil was most probably an open-chain derivative of the constitution given in one of the first three formulæ (see p. 14).

About 10 grams of the pure ketone was dissolved in about 100 c.c. of pure, dry ether, and a considerable quantity of phosphoric anhydride added to the solution; no reaction was observed even after keeping for about 24 hours at the ordinary temperature. The ethereal solution was filtered and evaporated, and the residual oil distilled under the ordinary pressure. It commenced to boil at about 193°, and almost the whole passed over between 203 and 206°, traces of a thick, yellowish oil, probably a condensation-product, remaining in the flask. The fraction 203—206° consisted of unchanged ketone, as was shown by its boiling point and other properties.

Action of Hydroxylamine and of Phenylhydrazine on Orthomethyltetrahydrobenzene Methyl Ketone.

The compound produced by the action of sulphuric acid on *αω*-diacetylpentane combines readily with hydroxylamine, yielding a colourless monoxime; it also forms a hydrazone-derivative when it is heated with phenylhydrazine.

Orthomethyltetrahydrobenzene Methyl Ketone-oxime,



$$CH_2<{{CH_2\cdot CMe} \atop {CH_2\cdot CH_2}}>C\cdot CMe{:}N\cdot OH.$$

Orthomethyltetrahydrobenzene methyl ketone-oxime is best prepared by treating the ketone with hydroxylamine by Auwers' method. About 15 grams of potash are dissolved in dilute alcohol, 5 grams of hydroxylamine hydrochloride added to the solution, and 10 grams of the ketone poured into the mixture. After being kept for about 24 hours, the whole is warmed gently on the water-bath until most of the alcohol has evaporated; it is then cooled, diluted with water, and slightly acidified with dilute hydrochloric acid. The yellowish oil which is precipitated is extracted with ether, the ethereal extract dried over calcium chloride, and evaporated.

The oxime remains as a yellowish oil which, after being kept over sulphuric acid under reduced pressure, is obtained in an almost pure condition, as is shown by the following analyses made with different samples of the crude product:—

I. 0·1640 gram gave 13·6 c.c. of nitrogen measured at 742 mm. and 20°.

II. 0·1560 gram gave 12·3 c.c. of nitrogen measured at 740 mm. and 20°.

	Calculated for $C_9H_{15}NO$.	Found.	
		I.	II.
N........	9·15 per cent.	9·23	8·86 per cent.

It is a thick, yellowish liquid, with a rather pleasant odour, and shows no signs of crystallising even when kept for a long time over sulphuric acid. It is insoluble or very sparingly soluble in cold, and only very slightly soluble in warm water, but it dissolves freely in potash and concentrated mineral acids, and it is miscible with alcohol, ether, &c., in all proportions. It dissolves in concentrated sulphuric acid with development of heat, yielding a clear yellow solution; on adding alkali to the diluted solution, no oil is precipitated, but on boiling the alkaline solution ammonia is evolved. It cannot be distilled under the ordinary pressure, as when heated, even in small quantities, it is completely decomposed.

Beckmann (*Berichte*, **20**, 2580) has shown that some oximes, under the influence of acetic chloride, glacial acetic acid, &c., undergo an intramolecular change, the group of atoms $C{:}N\cdot OH$ being converted into $CO\cdot NH$; the compounds thus produced are readily decomposed on hydrolysis into an amine and an acid.

Considerable quantities of the oxime of orthomethyltetrahydrobenzene methyl ketone were prepared in order to study its behaviour with Beckmann's reagents, as it was thought that in this way the constitution of the ketone might be ascertained.

For this purpose, 7 grams of the oxime was dissolved in 70 grams of glacial acetic acid and 14 grams of acetic anhydride, and the mixture, after having been saturated in the cold with hydrogen chloride, was heated at 100° for four or five hours in sealed tubes. At the end of this time, the solution had turned dark reddish-brown, but no separation of crystals occurred. On neutralising with sodium carbonate, a strong basic odour was perceptible, and a brownish-black oil separated at the surface of the solution. The oil was extracted with ether, and the ethereal extract dried and evaporated, when 5 grams of a dark-coloured oil remained; this was insoluble in water and in cold hydrochloric acid, but when heated with hydrochloric acid it was almost completely decomposed, yielding large quantities of resinous products and a small quantity of a yellow neutral oil which was not investigated very closely.

The sodium carbonate solution from which the oil had been extracted was rendered strongly alkaline with potash, and boiled for two hours, the distillate being collected in dilute hydrochloric acid. On adding platinic chloride to the dilute acid solution, a precipitate was produced, but this precipitate consisted of pure ammonium platinochloride, as was shown by its characteristic crystalline form, and also by the following analysis:—

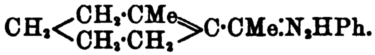
0·3865 gram of the platinochloride gave 0 1694 gram of platinum.

	Calculated for $(NH_3)_2H_2PtCl_6$.	Found.
Pt........	43·9 per cent.	43·83 per cent.

The experiment was repeated under similar conditions, but with the same results; a small quantity of a neutral oil was obtained, and the only basic product which could be isolated was ammonia.

When the oxime is treated with acetic chloride at the ordinary temperature, an extremely violent reaction occurs, and a dark-red solution is obtained. If the excess of acetic chloride is evaporated, and the residue is heated for a long time on the water-bath, it darkens in colour, and finally becomes black and very thick. A small quantity of a colourless crystalline compound can be isolated from this residue; this substance is insoluble in water, and only very sparingly soluble in ether; it does not give any basic odour when boiled with potash. It was not investigated, owing to the very small quantity at our disposal.

Orthomethyltetrahydrobenzene Methyl Ketone-hydrazone,



$$CH_2<\begin{matrix}CH_2\cdot CMe\\CH_2\cdot CH_2\end{matrix}>C\cdot CMe{:}N_2HPh.$$

The hydrazone-derivative of the ketone is best prepared by heating pure orthomethyltetrahydrobenzene methyl ketone with a slight excess of phenylhydrazine for two to three hours on the water-bath. The product is purified by dissolving it in ether, and washing the ethereal solution with dilute hydrochloric acid until it is free from phenylhydrazine. The solution is then dried over calcium chloride, the ether evaporated, and the residue kept for 24 hours over sulphuric acid under reduced pressure.

The analysis gave the following results:—

0·2218 gram of substance gave 24·95 c.c. of nitrogen measured at 18° and 740 mm.

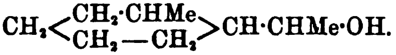
	Calculated for $C_{15}H_{20}N_2$.	Found.
N........	12·3 per cent.	12·3 per cent.

It is a thick, yellowish-brown oil, which shows no signs of crystallising; when left exposed to the air it gradually darkens in colour, and decomposes with evolution of gas. It is insoluble or only very sparingly soluble in water, but readily soluble in alcohol and ether.

REDUCTION OF ORTHOMETHYLTETRAHYDROBENZENE METHYL KETONE.

Methyltetrahydrobenzene methyl ketone yields three compounds when it is reduced with sodium in moist ethereal solution. When a large excess of sodium is employed, it is converted principally into orthomethylhexamethylene methyl carbinol, small quantities of a condensation-product being also formed. If only a slight excess of sodium is used, orthomethyltetrahydrobenzene methyl carbinol seems to be the principal product of the reaction.

Methylhexamethylene Methyl Carbinol,



$$CH_2{<}\begin{matrix}CH_2{\cdot}CHMe\\CH_2{-}CH_2\end{matrix}{>}CH{\cdot}CHMe{\cdot}OH.$$

Orthomethylhexamethylene methyl carbinol is prepared by treating pure methyltetrahydrobenzene methyl ketone with sodium in moist ethereal solution. The ketone is dissolved in about twenty times its volume of pure ether, the solution placed in a large bottle containing about 60 c.c. of water and provided with a reflux condenser, and small quantities of sodium are introduced from time to time. As soon as about 20 times the quantity of sodium theoretically necessary for complete reduction has been added, the ethereal solution is separated, and the residue extracted twice with ether. The ethereal solutions are mixed together, dried over potassium carbonate, filtered, and evaporated. A moderately thick, slightly yellow oil remains, the quantity of which is approximately equal to that of the ketone employed. On distilling it under 40 mm. pressure, the thermometer rises rapidly to 120°, and between this temperature and 280° the whole passes over. The fraction 120—280° is now repeatedly refractionated under reduced pressure (40 mm.), and is thus separated into a portion boiling at 127—137°, which consists of slightly impure methylhexamethylene methyl carbinol, and a portion boiling at about 250—260°. The higher boiling compound is only formed in comparatively small quantities, and will be again referred to.

The principal fraction, boiling at 127—137° (40 mm.), is again submitted to fractional distillation under reduced pressure, and finally under the ordinary pressure, the methylhexamethylene methyl carbinol being thus obtained in a pure state.

The analyses gave the following results :—

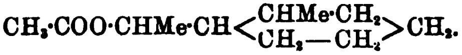
I. 0·1160 gram of substance gave 0·3221 gram of CO_2 and 0·1315 gram of H_2O.

II. 0·1494 gram of substance gave 0·4150 gram of CO_2 and 0·1685 gram of H_2O.

	Calculated for $C_9H_{18}O$.	Found.	
		I.	II.
C	76·06 per cent.	75·71	75·72 per cent.
H	12·66 „	12·59	12·53 „
O	11·27 „	11·70	11·75 „

Methylhexamethylene methyl carbinol is a thick, colourless oil with a smell very like that of menthol; it boils at 195—200° under the ordinary atmospheric pressure, and at 130—133° at 40 mm. without decomposition. It is only sparingly soluble in water, but miscible with alcohol, ether, &c., in all proportions. It dissolves in concentrated hydriodic acid with development of heat, and in a very short time the iodide separates from the solution.

Methylhexamethylene Methyl Carbinyl Acetate,



$$CH_3\cdot COO\cdot CHMe\cdot CH<\begin{matrix}CHMe\cdot CH_2\\ CH_2-CH_2\end{matrix}>CH_2.$$

Methylhexamethylene methyl carbinyl acetate is formed by treating methylhexamethylene methyl carbinol with acetic anhydride. The pure alcohol is boiled for 2 to 3 hours with excess of acetic anhydride in a flask provided with a reflux condenser; the excess of anhydride is then distilled off, and the residue is fractionated under the ordinary pressure. The thermometer rises rapidly to about 195°, almost the whole distilling between 200 and 210°. By fractionating the distillate two or three times, the acetate is obtained in a pure condition, as is shown by the following analysis :—

0·1541 gram of substance gave 0·4058 gram of CO_2 and 0·1567 gram of water.

	Calculated for $C_{11}H_{20}O_2$.	Found.
C	71·74 per cent.	71·75 per cent.
H	10·87 „	11·29 „
O	17·38 „	16·96 „

It is a colourless, mobile oil with a sweet rather pleasant odour, and boils at 204—208° under the ordinary pressure without decomposition. It is seemingly insoluble or only very sparingly soluble in water, but it is miscible with ether, alcohol, &c., in all proportions. When boiled with alcoholic potash, it is readily hydrolysed, being reconverted into the alcohol.

a-Iodoethylmethylhexamethylene,

$CH_2<\begin{matrix}CH_2\cdot CHMe\\ CH_2-CH_2\end{matrix}>CH\cdot CHMeI$.

Methylhexamethylene methyl carbinol dissolves in concentrated hydriodic acid, a considerable rise of temperature taking place, and after a very short time the iodide separates from the solution in the form of an oil. This compound is best prepared by heating the alcohol with excess of concentrated hydriodic acid (sp. gr. 1·96) at 180° in a sealed tube for about 4 hours. After diluting with water, the precipitated iodide is extracted with ether, the solution washed, first with water and then with very dilute sodium carbonate solution, until free from acid, then dried over calcium chloride, and evaporated. The residual oil can be easily obtained in a pure condition by submitting it to fractional distillation under reduced pressure.

An iodine determination by Carius' method gave the following result:—

0·2420 gram of substance gave 0·2270 gram of silver iodide.

	Calculated for $C_9H_{17}I$.	Found.
I........	50·29 per cent.	50·68 per cent.

Iodoethylmethylhexamethylene is a colourless mobile oil with an odour very like that of the iodides of the higher normal alcohols. It boils at 178–180° (110 mm.), seemingly without decomposition, and is insoluble in water, but readily soluble in the ordinary neutral organic solvents. It rapidly darkens on exposure to light.

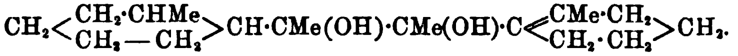
The fraction boiling at 240—260° (40 mm.), obtained in small quantities in the preparation of methylhexamethylene methyl carbinol, was distilled again under reduced pressure (50 mm.), and the portion passing over between 255—265° was collected separately. The analysis of this product gave results agreeing with the composition $C_{18}H_{32}O_2$.

0·2366 gram of substance gave 0·6655 gram of CO_2 and 0·2454 gram of H_2O.

	Calculated for $C_{18}H_{32}O_2$.	Found.
C........	77·14 per cent.	76·70 per cent.
H........	11·43 ,,	11·52 ,,

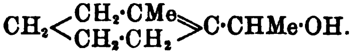
It is a very thick, yellowish oil with a peculiar aromatic odour, insoluble in water but miscible with alcohol, ether, &c., in all proportions.

No experiments have yet been made to ascertain the constitution of this compound, but it is most probably formed by the condensation of 1 mol. of orthomethyltetrahydrobenzene methyl ketone with 1 mol. of methylhexamethylene methyl ketone in a manner somewhat analogous to that in which pinacone is formed by the reduction of acetone, so that its constitution may be expressed by the formula—



$$\mathrm{CH_2}<\substack{\mathrm{CH_2\cdot CHMe}\\ \mathrm{CH_2 — CH_2}}>\mathrm{CH\cdot CMe(OH)\cdot CMe(OH)\cdot C}<\substack{\mathrm{CMe\cdot CH_2}\\ \mathrm{CH_2\cdot CH_2}}>\mathrm{CH_2}.$$

Methyltetrahydrobenzene Methyl Carbinol,



$$\mathrm{CH_2}<\substack{\mathrm{CH_2\cdot CMe}\\ \mathrm{CH_2\cdot CH_2}}>\mathrm{C\cdot CHMe\cdot OH}.$$

Orthomethyltetrahydrobenzene methyl carbinol is formed, as has been already stated, together with methylhexamethylene methyl carbinol when the ketone is reduced with a slight excess of the theoretical quantity of sodium in moist ethereal solution. It is obtained as follows:—Methyltetrahydrobenzene methyl ketone is dissolved in pure ether and treated with sodium under the conditions described in the preparation of the hexamethylene compound. After adding a little more sodium than is theoretically necessary, the ethereal solution is separated, dried over potassium carbonate, and evaporated. When the residual oil is carefully and repeatedly fractionated under reduced pressure (50 mm.), it is separated into two portions, the principal fraction, boiling at 141—143°, consisting of methyltetrahydrobenzene methyl carbinol, mixed possibly with small quantities of the hexamethylene-derivative and unchanged ketone.

It is a colourless, mobile oil, boils at 141—143° (50 mm.), and resembles methylhexamethylene methyl carbinol in its behaviour with solvents.

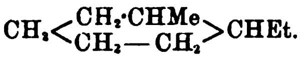
The following results were obtained on analysis:—

0·1599 gram of substance gave 0·4509 gram of CO_2 and 0·1703 gram of H_2O.

	Calculated for $C_9H_{16}O$.	Found.
C........	77·14 per cent.	76·90 per cent.
H........	11·43 "	11·83 "
O........	11·43 "	11·27 "

Reduction of Methylhexamethylene Methyl Carbinol.

Orthomethylethylhexamethylene,



$$CH_2<\begin{matrix}CH_2\cdot CHMe\\ CH_2—CH_2\end{matrix}>CHEt.$$

Orthomethylethylhexamethylene is the final product of the reduction of methyltetrahydrobenzene methyl ketone, and is obtained when methylhexamethylene methyl carbinol is reduced with hydriodic acid.

Its preparation is carried out as follows:—About 12 grams of the pure alcohol is heated with excess of fuming hydriodic acid for 2 – 3 hours in a flask provided with a reflux condenser, and, after diluting with water, the precipitated iodide is extracted with ether. The crude iodide, in quantities of about 3 grams, is heated in a sealed tube at 230—240° for 8 hours with a large excess of hydriodic acid of sp. gr. 1·96 and a little amorphous phosphorus. There is great pressure in the tube when cold, and the hydrocarbon forms a layer on the surface of the acid; this is separated from the acid, dried over potassium carbonate, and distilled. The thermometer rises rapidly to 120°, and the whole distils between 120 and 160°. The crude product is then repeatedly fractionated over sodium and finally over potassium. The hydrocarbon is thus obtained in a pure state and on analysis gave the following results:—

I. 0·1211 gram of substance gave 0·3795 gram of CO_2 and 0·1590 gram of H_2O.

II. 0·1100 gram of substance gave 0·3450 gram of CO_2 and 0·1434 gram of H_2O.

	Calculated for C_9H_{18}.	Found. I.	Found. II.
C......	85·7 per cent.	85·47	85·54 per cent.
H......	14·3 „	14·58	14·47 „

A vapour-density determination made by Hofmann's method in the vapour of aniline gave the following results:—

0·0502 gram of substance yielded 57·0 c.c. of vapour. Temperature of vapour 184°. Bar. 765 mm. Difference of level 582 mm. Temperature of air 15°.

	Calculated for C_9H_{18}.	Found.
Molecular weight....	126	125

Orthomethylethylhexamethylene is a colourless, very mobile oil, the odour of which cannot be distinguished from that of the liquid paraffins. It boils at 150—152° and is insoluble in water and concentrated hydriodic acid, but miscible with ether, alcohol, &c., in all proportions. When treated with cold concentrated nitric acid, oxidation quickly commences and the mixture becomes very hot. A small quantity of the hydrocarbon was treated with nitric acid in the cold; as soon as the first energetic reaction was at an end, the mixture was heated on the water-bath in a flask provided with a reflux condenser. The hydrocarbon gradually disappeared, dense, brown fumes being evolved, and finally a homogeneous liquid was obtained. The solution remained clear on adding water, and on evaporation it yielded only a very small quantity of a thick, syrupy residue which was not investigated owing to the small amount of material at our disposal.

CONDENSATION-PRODUCTS OF *aω*-DIACETYLPENTANE.

A small quantity of two condensation-products are obtained in the preparation of diacetylpentane by the hydrolysis of ethyl diacetylcaproate (Trans., 1889, **55**, 333); these products remain in the form of a thick brown oil when the crude diacetylpentane is distilled under reduced pressure. The residues obtained in this way from several operations were mixed together and submitted to fractional distillation under a pressure of 35 mm. The thermometer rose rapidly to about 230°, and between about 250 and 280° a considerable proportion of the oil distilled; the temperature then rose quickly to 310°, the remainder passing over between 310° and 340°.

The portion collected between 250 and 280° was fractionated two or three times under the same pressure, and in this way a yellow oil boiling at 265—275° was obtained.

The analysis of this compound gave the following results:—

I. 0·1418 gram substance gave 0·4030 gram of CO_2 and 0·1329 gram of H_2O.

II. 0·1118 gram of substance gave 0·3190 gram of CO_2 and 0·1047 gram of H_2O.

	Calculated for $C_{18}H_{28}O_2$.	Found. I.	Found. II.
C........	78·26 per cent.	77·82	77·70 per cent.
H........	10·14 „	10·40	10·30 „
O........	11·60 „	11·78	12·00 „

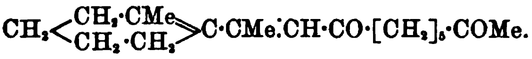
A molecular weight determination was carried out by Raoult's method in glacial acetic acid solution and resulted as follows:—

Freezing point of the acetic acid 15·740°.

1·4882 gram of substance dissolved in 67·25 grams of acetic acid lowers the freezing point 0·30°.

	Calculated for $C_{18}H_{28}O_2$.	Found.
Molecular weight	276	287

These results show that this condensation product is formed by the combination of 2 mols. of diacetylpentane with elimination of 2 mols. of water; as the diketone is readily converted into methyltetrahydrobenzene methyl ketone with elimination of 1 mol. of water, the constitution of the compound $C_{18}H_{28}O_2$ is most probably expressed by the formula—



$$CH_2{<}\begin{matrix}CH_2\cdot CMe\\ CH_2\cdot CH_2\end{matrix}{>}C\cdot CMe{:}CH\cdot CO\cdot[CH_2]_5\cdot COMe.$$

It is a yellowish, very thick oil, boiling at 265—275° (35 mm.) seemingly without decomposition, and it shows no signs of crystallising even when kept for a long time in a desiccator under reduced pressure. It is miscible with alcohol, ether and other neutral solvents in all proportions, but it is insoluble in water.

The other fraction, boiling at 310—340° (35 mm.), which is obtained from the residues in the preparation of diacetylpentane was likewise submitted to fractional distillation, and in this way a yellow oil boiling at 320—330° can be isolated without much difficulty.

This compound gave the following results on analysis:—

0·1988 gram of substance gave 0·5702 gram of CO_2 and 0·1828 gram of H_2O.

	Calculated for $C_{27}H_{42}O_3$.	Found.
C	78·26 per cent.	78·22 per cent.
H........	10·14 „	10·20 „
O	11·60 „	11·58 „

It is a yellow oil with a slight aromatic odour, and resembles the preceding compound in its behaviour with solvents; it is of an almost syrupy consistency, but shows no signs of crystallising when kept for a long time in a desiccator under reduced pressure.

The higher boiling point of this compound indicates a more complicated constitution than that of the condensation-product described above, and it is probably formed by the combination of 3 mols. of diacetylpentane, with elimination of 3 mols. of water, according to the equation, $3C_9H_{16}O_2 = C_{27}H_{42}O_3 + 3H_2O$.

Action of Dehydrating Agents on αω-Dibenzoylpentane.

The investigation of the behaviour of dibenzoylpentane with dehydrating and reducing agents has been commenced and has already led to interesting results, but the compounds obtained have not yet been examined very fully. A very short account of some of our experiments may, however, be suitably given in this paper on account of their bearing on the question of the constitution of methyltetrahydrobenzene methyl ketone.

Concentrated sulphuric acid seems to have no dehydrating action on dibenzoylpentane in the cold, as is shown by the following experiment. About 0·5 gram of the pure diketone was dissolved in concentrated sulphuric acid, and the solution kept at the ordinary temperature for three days; it gradually became violet in colour and a small quantity of sulphurous anhydride was evolved. The addition of water caused the precipitation of a colourless compound, which, after recrystallisation from dilute methyl alcohol, melted at 66—67°, and was found to consist of unchanged dibenzoylpentane; the quantity obtained was about 0·46 gram.

When dibenzoylpentane is warmed with phosphoric anhydride it is converted into a compound having the composition $C_{19}H_{18}O$, but considerable quantities of resinous products are also formed.

The compound $C_{19}H_{18}O$ crystallises from alcohol in beautiful, colourless needles, melting at 110—111°.

An analysis gave the following results:—

0·1187 gram of substance gave 0·3787 gram of CO_2 and 0·0744 gram of H_2O.

	Calculated for $C_{19}H_{18}O$.	Found.
C........	87·02 per cent.	86·84 per cent.
H........	6·87 „	6·96 „
O........	6·11 „	6·20 „

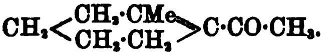
This substance is at present under investigation, and will form the subject of a paper which we hope soon to be able to communicate to the Society.

Heriot Watt College,
Edinburgh.

V.—*αω-Diacetyl-αω-diethylpentane.*

By F. Stanley Kipping, Ph.D., DSc., and W. H. Perkin, jun., Ph.D.

In the preceding paper we have described the preparation of a compound of the composition $C_9H_{14}O$, and have given an account of various experiments, from the results of which it seems to be proved that this substance is methyltetrahydrobenzene methyl ketone,



$$CH_2{<}\genfrac{}{}{0pt}{}{CH_2\cdot CMe}{CH_2\cdot CH_2}{>}C\cdot CO\cdot CH_3.$$

In order to distinguish between several of the theoretically possible formulæ for this compound (compare p. 14), it became necessary to prepare a diketone of the formula $R\cdot CO\cdot CHR\cdot[CH_2]_3\cdot CHR\cdot CO\cdot R$, and to study its behaviour under the same conditions as those employed in the preparation of the compound $C_9H_{14}O$ from *αω*-diacetylpentane, $COMe\cdot[CH_2]_5\cdot COMe$.

A short account of these experiments will, we hope, not be without some interest.

When ethyl ethylacetoacetate (2 mols.) is treated with sodium ethoxide (2 mols.) and trimethylene bromide (1 mol.) in alcoholic solution, a moderately energetic reaction occurs on warming gently, and, after proceeding in the usual manner, a yellow oil is obtained.

The crude product, which consists of several compounds, contains about 40—45 per cent. of ethyl *αω*-diacetyl-*αω*-diethylpimelate, $COOEt\cdot CEt(COMe)\cdot[CH_2]_3\cdot CEt(COMe)\cdot COOEt$, produced by the combination of 1 mol. of trimethylene bromide with 2 mols. of ethyl sodioethylacetoacetate in accordance with the equation—

$$2CH_3\cdot CO\cdot CNaEt\cdot COOEt + C_3H_6Br_2 = COOEt\cdot CEt(COMe)\cdot[CH_2]_3\cdot CEt(COMe)\cdot COOEt + 2NaBr.$$

This ethereal salt is readily hydrolysed when boiled with alcoholic potash, the principal products being *αω*-diacetyl-*αω*-diethylpentane and *ω*-acetyl-*αω*-diethylcaproic acid. The equations representing the decomposition are as follows :—

$$COOEt\cdot CEt(COMe)\cdot[CH_2]_3\cdot CEt(COMe)\cdot COOEt + 4KOH = COMe\cdot CHEt\cdot[CH_2]_3\cdot CHEt\cdot COMe + 2K_2CO_3 + 2C_2H_5\cdot OH,$$

and

$$COOEt\cdot CEt(COMe).[CH_2]_3\cdot CEt(COMe)\cdot COOEt + 4KOH = COMe\cdot CHEt\cdot[CH_2]_3\cdot CHEt\cdot COOK + 2C_2H_5\cdot OH + K_2CO_3 + CH_3\cdot COOK.$$

It seems probable that, in addition to the two compounds referred to above, small quantities of αω-diethylpimelic acid are also produced by the following reaction:—

$$\mathrm{COOEt{\cdot}CEt(COMe){\cdot}[CH_2]_3{\cdot}CEt(COMe){\cdot}COOEt + 4KOH =}$$
$$\mathrm{COOK{\cdot}CHEt{\cdot}[CH_2]_3{\cdot}CHEt{\cdot}COOK + 2C_2H_5{\cdot}OH + 2CH_3{\cdot}COOK.}$$

Action of Trimethylene Bromide on Ethyl Sodioethylacetoacetate.

Formation of Ethyl αω-Diacetyl-αω-diethylpimelate, $\mathrm{COOEt{\cdot}CEt(COMe){\cdot}[CH_2]_3{\cdot}CEt(COMe){\cdot}COOEt}$.

Ethyl diacetyldiethylpimelate is obtained, together with considerable quantities of compounds of lower boiling point, when ethyl sodioethylacetoacetate is treated with an alcoholic solution of trimethylene bromide.

Ethyl ethylacetoacetate (2 mols.) is added, in small quantities at a time, to a solution of sodium (1 mol.) in about 12 times its weight of alcohol, the temperature being kept below 25—30° by cooling under the tap from time to time; after adding the trimethylene bromide (1 mol.), the mixture is heated on the water-bath in a flask provided with a reflux condenser. As soon as the temperature rises to about 70—80°, an energetic reaction commences, sodium bromide separates from the solution, and the heat developed is sufficient to keep the alcohol in ebullition for several minutes. After heating for 2—3 hours to complete the reaction, the alcohol is evaporated, the residue mixed with water, and the precipitated oil extracted with ether. When the ethereal extract is evaporated, there remains a yellow oil, the quantity of which is about equal to that of the ethyl ethylacetoacetate employed.

The crude product is distilled with steam as quickly as possible, the distillation being continued as long as oily drops collect in the receiver. In this way the ethyl diacetyldiethylpimelate, which forms from 40 to 45 per cent. of the whole, is separated from the more volatile compounds. The dark yellow oil which remains in the flask is extracted with ether, the ethereal solution dried over calcium chloride and evaporated. That this process of separation is very efficient is shown by the following analysis, which was made with a portion of the residual oil after it had been kept over sulphuric acid under reduced pressure for about 24 hours.

0·1474 gram of substance gave 0·3430 gram of CO_2 and 0·1220 gram of H_2O.

	Calculated for $C_{19}H_{32}O_6$.	Found.
C	64·05 per cent.	63·46 per cent.
H	8·99 ,,	9·22 ,,
O	26·96 ,,	27·32 ,,

When the crude ethyl diacetyldiethylpimelate is distilled under reduced pressure (45—50 mm.), the thermometer rises rapidly to about 205°, then a little more slowly to 235°; almost the whole distils between 235° and 255°, a small quantity only passing over between 255° and 280°. The oil boiling at 235—255° was fractionated again under the same pressure, and the portion boiling constantly at 249—252° collected separately.

This fraction quickly solidifies to a mass of colourless crystals, and after having been spread on a porous plate to free it from traces of oily impurities, it melted at 42—43° with previous softening.

The analyses of the crystalline compound purified in this way gave the following results :—

I. 0·2109 gram of substance gave 0·4937 gram of CO_2 and 0·1689 gram of H_2O.

II. 0·2500 gram of substance gave 0·5840 gram of CO_2 and 0·2016 gram of H_2O.

	Calculated for $C_{19}H_{32}O_6$.	Found. I.	Found. II.	
C	64·05 per cent.	63·80	63·71	per cent.
H	8·99 ,,	8·90	8·96	,,
O	26·96 ,,	27·30	27·33	,,

Ethyl diacetyldiethylpimelate separates from ether and alcohol in long, very slender needles melting at 44—45° with slight previous softening; it is very readily soluble both in ether and in alcohol, so that it cannot well be purified by crystallisation from these solvents. On adding water to a cold alcoholic solution, the ethereal salt is precipitated in an oily condition, but it almost immediately solidifies to a mass of ill-defined crystals. It is very readily soluble in benzene, light petroleum, xylene, chloroform, and most ordinary solvents, but it seems to be quite insoluble in cold water. Ferric chloride produces no coloration in alcoholic solutions. It is readily hydrolysed by warm alcoholic potash, the principal product being acetyldiethylcaproic acid. When treated with concentrated alcoholic potash in the cold, it is slowly decomposed; the solution contains small quantities of diacetyldiethylpentane, and the potassium salt of a thick, colourless acid, probably diacetyldiethylpimelic acid, which is mixed with some other acid richer in carbon.

Bye-products obtained in the preparation of Ethyl Diacetyldiethylpimelate.

The crude product of the action of trimethylene bromide on ethyl sodioethylacetoacetate contains, as has been stated above, a considerable proportion (55—60 per cent.) of an oil which can be separated from the ethyl diacetyldiethylpimelate by distilling with steam; when the distillate is extracted with ether, and the extract dried over calcium chloride and evaporated, a yellowish, mobile oil with a pleasant ethereal odour is obtained. This oil is probably a mixture of unchanged ethyl ethylacetoacetate and ethyl ethylallylacetoacetate; the last-named compound would probably be produced by the interaction of the trimethylene bromide and ethyl sodioethylacetoacetate according to the equations—

$$CH_3\cdot CO\cdot CEtNa\cdot COOEt + C_3H_6Br_2 = CH_3\cdot CO\cdot CEt\cdot(COOEt)\cdot CH_2\cdot CH_2\cdot CH_2Br \text{ and}$$

$$CH_3\cdot CO\cdot CEt(COOEt)\cdot CH_2\cdot CH_2\cdot CH_2Br + CH_3\cdot CO\cdot CEtNa\cdot COOEt = CH_3\cdot CO\cdot CEt(COOEt)\cdot CH_2\cdot CH{:}CH_2 + CH_3\cdot CO\cdot CHEt\cdot COOEt + NaBr.$$

It was repeatedly submitted to fractional distillation under the ordinary pressure in order to try and isolate the ethyl ethylallylacetoacetate, but the attempt was unsuccessful. Various fractions were analysed, but in all cases the results agreed with those required by a mixture of ethyl ethylacetoacetate and ethyl ethylallylacetoacetate, the analyses giving from 64·4 to 65·3 per cent. of carbon and about 9·1 per cent. of hydrogen instead of 66·7 per cent. of carbon and 9·0 per cent. of hydrogen as required by ethyl ethylallylacetoacetate.

αω-Diacetyl-αω-diethylpentane, $CH_3\cdot CO\cdot CHEt\cdot[CH_2]_3\cdot CHEt\cdot CO\cdot CH_3$

Diacetyldiethylpentane is best prepared by treating ethyl diacetyldiethylpimelate with alcoholic potash as described in the preparation of diacetylpentane.

The ethereal salt is dissolved in a small quantity of alcohol, and the solution heated to boiling in a flask provided with a reflux condenser; about one-third of a hot, moderately concentrated, alcoholic solution of potash (4 mols.) is then added, and the mixture is boiled again. As soon as no further separation of potassium carbonate occurs, another third of the potash solution is poured in and the mixture is heated again for about 10 minutes; the remainder of the alcoholic potash is then added and the alcohol is immediately evaporated. The alkaline residue is mixed with water, the precipitated diketone extracted with ether, the ethereal solution dried over potassium carbonate and evaporated. The yellowish-brown, mobile oil which is thus obtained consists of impure diacetyldiethylpentane; the quantity of the crude product is only 11—12 grams from 50 grams of the ethereal salt, the small yield being due to the formation of large quantities of acid decomposition-products.

As the crude diketone showed no signs of crystallisation even when cooled below 0°, it was submitted to fractional distillation under a pressure of 110 mm. The thermometer rose rapidly to about 160°, and about 10 per cent. of the whole distilled below 206°; the thermometer then remained very constant at 207—208°, about 50 per cent. passing over between 200° and 210°, and the remainder at a slightly higher temperature.

The fraction 200—210° was distilled again under the same pressure and the portion boiling at 207—208° collected separately. This liquid on analysis gave the following results:—

0·1690 gram of substance gave 0·4533 gram of CO_2 and 0·1751 gram of H_2O.

	Calculated for $C_{13}H_{24}O_2$.	Found.
C........	73·59 per cent.	73·10 per cent.
H........	11·32 „	11·32 „
O........	15·09 „	15·58 „

Diacetyldiethylpentane is a colourless, moderately mobile oil with a slight, rather pleasant, aromatic odour similar to that of diacetylpentane. It boils at 207—208° (110 mm.), and shows no signs of crystallising. It is insoluble or only very sparingly soluble in water, but miscible with alcohol, ether, and other ordinary solvents in all proportions. It does not combine with sodium hydrogen sulphite even when left for a long time in contact with a concentrated aqueous solution of the salt. It dissolves in cold concentrated sulphuric acid with a yellowish-brown coloration, but it undergoes no change even after two days' time, as is proved by the experiments described below.

αω-Diacetyl-αω-diethylpentanedioxime,

$NOH{:}CMe{\cdot}CHEt{\cdot}[CH_2]_3{\cdot}CHEt{\cdot}CMe{:}NOH$.

Diacetyldiethylpentane combines readily with hydroxylamine in alkaline solution, yielding the dioxime.

The diketone (about 1 gram) is dissolved in alcohol, treated with an alcoholic solution of hydroxylamine hydrochloride (1·5 gram) and potash (5 grams), and the mixture kept at the ordinary temperature for 24 hours; the alcohol is then partially evaporated on the water-bath, the residue mixed with water and treated with a slight excess of dilute hydrochloric acid. The oil which is precipitated is extracted with ether, and after drying the extract over calcium chloride, the ether is evaporated. The dioxime remains in the form of a thick, yellowish oil which soon solidifies to a mass of crystals. After removing oily impurities by spreading the crystals on a porous plate, a nitrogen determination was made with the following result:—

0·1184 gram of substance gave 12 c.c. of nitrogen measured at 12° and 755 mm. pressure.

	Calculated for $C_{13}H_{26}N_2O_2$.	Found.
N	11·6 per cent.	11·9 per cent.

Diacetyldiethylpentanedioxime separates from a mixture of benzene and light petroleum in colourless, microscopic crystals melting at 110—111°. It is readily soluble in alcohol, ether, acetic acid, benzene, and other ordinary solvents, but only very sparingly in cold light petroleum; on adding light petroleum to the benzene solution, the dioxime is precipitated in a crystalline condition. It dissolves freely in alkalis and in moderately concentrated mineral acids.

Behaviour of Diacetyldiethylpentane with Concentrated Sulphuric Acid.

The chief object in view in preparing diacetyldiethylpentane was to study its behaviour with sulphuric acid. It has been shown in the previous paper that diacetylpentane dissolves in cold concentrated sulphuric acid, and is thereby converted into a compound $C_9H_{14}O$; the various theoretically possible formulæ for this compound have been already discussed, and it has been shown that its constitution is probably that of an orthomethyltetrahydrobenzene methyl ketone. One of the chief arguments in support of this view is the fact that diacetyldiethylpentane does not yield an analogous product under the same conditions, and is, in fact, unchanged by concentrated sulphuric acid.

About 8 grams of crude diacetyldiethylpentane was dissolved in about 60 grams of concentrated sulphuric acid; a slight development of heat was observed and the solution gradually turned brown. After keeping for about 24 hours, the solution was poured into a large volume of cold water and the precipitated oil extracted with ether. A yellowish-brown oil remained when the ether was evaporated, and the weight of this product was about 6·5 grams. The crude oil was submitted to fractional distillation under the ordinary pressure; the thermometer rose rapidly to 230°, and only a small quantity distilled between 230° and 240°, the greater portion passing over at 245—255°.

This fraction was collected separately, and analysed without any further purification. The following results were obtained:—

0·2228 gram of substance gave 0·5863 gram of CO_2 and 0·2239 gram of H_2O.

	Calculated for		Found.
	$C_{13}H_{22}O$.	$C_{13}H_{24}O_2$.	
C	80·4	73·6 per cent.	71·7 per cent.
H	11·3	11·3 „	11·2 „
O	11·3	15·1 „	17·1 „

This analysis shows that the fraction boiling at 245—255° consisted of impure diacetyldiethylpentane, and proves conclusively the absence of any compound richer in carbon. Since this fraction formed about 60 per cent. of the crude product, and most of the remainder boiled at a temperature above 255°, the experiment would show that the formation of a compound $C_{13}H_{22}O$ does not take place under these conditions.

In order to prove beyond doubt that such is really the case, the experiment was repeated in the following manner:—10 grams of almost pure diacetyldiethylpentane was dissolved in 300 grams of cold concentrated sulphuric acid and the solution kept for two days at the ordinary temperature; there was only a slight evolution of sulphurous anhydride, but the solution gradually darkened in colour. It was poured into a large volume of cold water, the oil extracted with ether, the extract dried over potassium carbonate and evaporated; the residual oil weighed about 8·8 grams. When the oil was distilled under the ordinary pressure, the thermometer rose at once to 215°, and the whole passed over between 215—270°, the greater portion boiling at about 250°. The fraction 215—270°, that is to say, the whole of the crude product, was distilled again under the ordinary pressure, and the portions passing over at 215—225° and 225—235° were collected separately. These two fractions were analysed with the following results:—

I. Fraction boiling at 215—225°: 0·1568 gram of substance gave 0·4141 gram of CO_2 and 0·1617 gram of H_2O.

II. Fraction boiling at 225—235°: 0·1654 gram of substance gave 0·4371 gram of CO_2 and 0·1733 gram of H_2O.

	Calculated for		Found.	
	$C_{13}H_{22}O$.	$C_{13}H_{24}O_2$.	I.	II.
C	80·4 p. c.	73·5 p. c.	72·06	72·5 p. c.
H	11·3 „	11·3 „	11·40	11·6 „
O	11·3 „	15·2 „	16·64	15·9 „

These analyses show that both fractions consisted of impure diacetyldiethylpentane, the purer of the two being naturally that of higher boiling point, as it approaches more closely that of the pure diketone. Now, since, if any dehydrating action had occurred, the resulting compound must have been contained in these two lowest boiling portions of the crude oil, it is clear that no compound of the composition $C_{13}H_{22}O$ had been formed.

This experiment, therefore, confirms the previous results and proves conclusively that diacetyldiethylpentane is not converted into a compound of the composition $C_{13}H_{22}O$ under conditions which, in the case of diacetylpentane, result in the formation of a compound of the composition $C_9H_{14}O$; this difference in behaviour can be explained only by assuming that the latter has the constitution of an orthomethyltetrahydrobenzene methyl ketone, a view which is fully borne out by other experiments.

ω-Acetyl-αω-diethylcaproic Acid, $CH_3 \cdot CO \cdot CHEt \cdot [CH_2]_3 \cdot CHEt \cdot COOH$.

The alkaline mother-liquors from which the diacetyldiethylpentane has been extracted with ether contain the potassium salts of acetyldiethylcaproic acid, acetic acid, and probably also diethylpimelic acid; these compounds having been produced by the hydrolysis of ethyl diacetyldiethylpimelate in accordance with the equations given on pp. 29 and 30. On acidifying with dilute sulphuric acid, a thick, yellowish oil is precipitated; the solution is shaken three or four times with ether, the ethereal extract dried over calcium chloride, and the ether evaporated. As the thick, sour-smelling oil which remained showed no signs of crystallising even when cooled below 0°, it was submitted to fractional distillation under reduced pressure (110 mm.). The acetic acid which passed over at the commencement of the distillation was readily identified by its odour and by converting it into ethyl acetate; the thermometer then rose rapidly to 200°, a small quantity only distilled below 240°, and the whole of the remainder passed over between 240° and 280°. The portion boiling at 240—280° was fractionated again under a pressure of 90 mm., and a fairly large quantity, boiling at 253—255°, collected separately.

The analysis of this fraction (b. p. 253—255°) showed that it consisted of acetyldiethylcaproic acid:

0·1420 gram of substance gave 0·3490 gram of CO_2 and 0·1305 gram of H_2O.

	Calculated for $C_{12}H_{22}O_3$.	Found.
C	67·28 per cent.	67·03 per cent.
H	10·28 „	10·21 „
O	22·43 „	22·76 „

Acetyldiethylcaproic acid is a thick, colourless liquid having an odour very like that of pyruvic acid; it becomes semi-solid when cooled strongly, but it has not yet been obtained in a crystalline condition. It is insoluble, or only very sparingly soluble, in water, but miscible with alcohol, ether, benzene, and other ordinary solvents in all proportions.

The *silver* salt, $CH_3{\cdot}CO{\cdot}CHEt{\cdot}(CH_2)_3{\cdot}CHEt{\cdot}COOAg$, was prepared by dissolving a portion of the fraction boiling at 253—255° in ammonia, and fractionally precipitating the neutral solution with silver nitrate. It is a colourless, seemingly amorphous compound, and rather sparingly soluble in hot water; it seems to be stable in the light.

A silver determination, made with a portion of the second fraction of the salt, gave the following result:—

0·4714 gram of substance gave 0·1605 gram of silver.

	Calculated for $C_{12}H_{21}O_3Ag$.	Found.
Ag	33·64 per cent.	34·03 per cent.

The first fraction gave a somewhat larger percentage of silver probably owing to the presence of small quantities of diethylpimelic acid.

In neutral aqueous solutions of the ammonium salt, lead acetate and mercuric chloride produce a colourless precipitate; ferric chloride, a buff-coloured precipitate; and copper sulphate, a dark-green precipitate.

The calcium salt and the barium salt are readily soluble in water.

ω-Acetyl-αω-diethylcaproic Acid Oxime,
$NOH{:}CMe{\cdot}CHEt{\cdot}[CH_2]_3{\cdot}CHEt{\cdot}COOH$.

Acetyldiethylcaproic acid oxime can be obtained by treating the acid with hydroxylamine hydrochloride and excess of potash in dilute alcoholic solution; after keeping for about 24 hours, the alcohol is evaporated on the water-bath, the residue dissolved in water, the solution slightly acidified with hydrochloric acid, and extracted with ether. The crude product is a thick, yellowish oil, but it slowly solidifies to a mass of crystals; the crystalline substance, after having been spread on a porous plate and washed with a little light petroleum, melted at 102—103°.

A nitrogen determination gave the following result:—

0·0961 gram of substance gave 5·05 c.c. of nitrogen measured at 14° and 745 mm. pressure.

	Calculated for $C_{12}H_{23}NO_3$.	Found.
N........	6·11 per cent.	6·12 per cent.

Acetyldiethylcaproic acid oxime crystallises from a mixture of benzene and light petroleum in colourless, microscopic plates; it is readily soluble in alcohol and benzene, but only sparingly in light petroleum, and, seemingly, insoluble in water; it dissolves freely in alkalis and in concentrated hydrochloric acid.

Heriott-Watt College, Edinburgh,
Chemical Laboratory.

VI.—*Frangulin.*

By T. E. Thorpe, F.R.S., and H. H. Robinson, M.A.

The constituents of the bark of the Alder Buckthorn (*Rhamnus frangula*), and more especially the yellow colouring matters that can be got from it, have occupied the attention of several chemists since the beginning of the century. Prior to 1857, no ultimate analyses of these colouring matters were made, although the substances obtainable from the bark had been frequently described. Gerber, in 1828 (*Brande's Archiv. f. Pharm.*, **26**, 1), published a proximate analysis of the bark, and among the substances enumerated was a yellow resinous colouring matter, which with alkalies gave a dark-red colour. Binswanger, in 1850, published a work on the constituents of the bark (*Pharm. Studien über R. frangula und cathartica. München;* also in *Buchner's Repertorium f. Pharm.* [3], **4**, 47); among these he mentions a yellow colouring matter which he states Buchner had examined and named *Rhamno-Xanthin.* Buchner's work was not published until some years later, namely, in 1853 (*Annalen*, **87**, 218); he had noticed that the paper in which some of the root-bark had been wrapped was coloured yellow, and that the inner surface of the bark was covered with golden-yellow crystals. He prepared some of the substance, examined its properties, and described its points of resemblance and dissimilarity to chrysophanic acid. In a later paper (*Zeitschrift für Chem.*, 1865, 699), he described some yellowish-red, needle-shaped crystals he got from Rhamno-Xanthin by sublimation, but gave no analyses.

Winckler (*Archiv. der Pharm.*, 1856, 335), Phipson (*Compt. rend.*, **47**, 153), Salm Horstmar (*Pogg. Ann.*, **109**, 539), and Enz (*Viertel-*

jahrschrift für Pharm., **16**, 106) have also treated of these yellow colouring matters.

Casselmann, in 1857 (*Annalen*, **104**, 77), was the first to publish an ultimate analysis of a yellow colouring matter got from *R. frangula*. This substance he named *Frangulin*, considering that Buchner's name Rhamno-Xanthin was liable to be confused with Xantho-rhamnin, a substance Kane had obtained from *R. cathartica* and *tinctoria*. He used ammonia-water to extract it from the bark, and describes it as forming lemon-yellow, crystalline masses with a slight silky lustre and as appearing under the microscope in bright-yellow, transparent, square tables. He gives the melting point as about 249°. He made three analyses of frangulin prepared by different methods and dried at 100°; the mean of these analyses was, carbon 57·19 per cent. and hydrogen 4·98 per cent., from which he deduced the formula $C_6H_6O_3$ (new notation). He examined the action of fuming nitric acid on frangulin, and concluded that it yielded oxalic acid and a nitro-derivative; this he analysed, together with its silver and copper salts, and assigned to it the formula $C_{20}H_{10}O_8(NO_2)_5 + \frac{1}{2}H_2O$.

Kubly, in 1866 (*Pharm. Zeitschrift für Russland*, **5**, 160), obtained a substance from the bark which he named *Avornin*, and which he found to be a glucoside, yielding on hydrolysis, sugar, an acid which he called avornic acid, and an amorphous resin.

Faust repeated his work and found that avornin was impure frangulin, but to Kubly is due the discovery of the glucosidal nature of frangulin.

Faust, in 1872, published a paper (*Annalen*, **165**, 229) on frangulin and frangulic acid: he prepared a small quantity of frangulin, using alcohol to extract it from the bark; he did not see the square tables mentioned by Casselmann, and found that its melting point was 226°, also that when boiled with hydrochloric acid it split up into frangulic acid and sugar; but he had not enough frangulin either to make a quantitative hydrolysis or an analysis. He accepted Casselmann's analysis, and multiplying $C_6H_6O_3$ by $3\frac{1}{3}$, gave $C_{20}H_{20}O_{10} = C_{14}H_8O_4 + C_6H_{12}O_6$ as the equation representing its hydrolysis. He prepared frangulic acid directly from the bark, using boiling caustic soda solution; he found that on drying this at 120° it lost 6·07 per cent. in one case and 6·4 per cent. in another, and when thus dried gave carbon 67·26 per cent. and hydrogen 4 per cent. as a mean of five analyses: but in these the carbon varied from 66·78 to 67·91 per cent. He assigned the formula $2C_{14}H_8O_4,3H_2O$ to the undried substance and $2C_{14}H_8O_4,H_2O$ to it when dried at 120°. He next dried a sample at 180°, when it lost 10·97 per cent. ($2C_{14}H_8O_4,3H_2O$ in losing $3H_2O$ would give up 10·11 per cent.), and on analysing the product thus dried he got carbon 70·33 per cent. and hydrogen 3·67 per cent.

($C_{14}H_8O_4$ would give carbon 70 per cent. and hydrogen 3·3 per cent.). He further prepared and analysed a bromine-derivative and an acetyl-derivative of frangulic acid. By distilling frangulic acid with zinc-dust he obtained anthracene, and concluded that the acid was *dihydroxyanthraquinone* and therefore an isomer of alizarin.

Liebermann and Waldstein were the next authors to treat of the yellow colouring matter got from *R. frangula* (*Berichte*, 1876, 1775); they did not prepare frangulin, but examined a colouring matter got from the bark by means of caustic soda solution. They made five analyses of this; in two cases drying the substance at 190°, and in one case subliming it, crystallising the sublimate from alcohol and drying at 150°. The mean of their analyses was, carbon 67·1 per cent. and hydrogen 4 per cent., the carbon ranging from 66·7 to 67·2 per cent.; they therefore assigned the formula $C_{15}H_{10}O_5$ to the substance. They prepared and analysed an acetyl-derivative and made a distillation of the colouring matter with zinc-dust, obtaining a mixture of anthracene and methylanthracene, resembling that obtained from emodin and from chrysophanic acid, and giving on oxidation *anthraquinonecarboxylic acid.* They compared the properties of the colouring matter and its behaviour with various reagents with those of emodin, and they found the melting point of both to be 257°. Finally, they concluded that the colouring matter they examined was identical with emodin. As regards Faust's frangulic acid, they considered it to be probably a different substance, and that possibly it and emodin may occur jointly in the bark and mutually replace one another as alizarin and purpurin do in madder. They suggest $C_{21}H_{20}O_{10} + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_6$ as the equation representing the hydrolysis of frangulin.

Keussler, who published his paper in 1878 (*Pharm. Zeitschrift für Russland*, **17**, 257), did not prepare frangulin, but used caustic soda and sodium carbonate in his operations on the bark, and obtained a substance having the same external appearances as the frangulic acid of Faust and the emodin of Liebermann and Waldstein. He came to the conclusion, however, that this was not emodin, but contained an additional CH_2 group, and was *trihydroxyethyl-* or *trihydroxydimethylanthraquinone.* He made five analyses of it dried at 180°, and obtained carbon 67·54 per cent. and hydrogen 4·38 per cent. as a mean result, the carbon varying from 67·41 to 67·69 per cent. ($C_{16}H_{12}O_5$ corresponds to carbon 67·6 per cent. and hydrogen 4·2 per cent.). On distilling it with zinc-dust, he obtained and analysed a mixture of anthracene and methylanthracene, a considerable evolution of gas taking place during the distillation, possibly due to the decomposition of dimethylanthracene. He also prepared and analysed a nitro-derivative and its silver salt.

The only analysis of frangulin since that of Casselmann was made by Schwabe (*Arch. der Pharm.*, 1888, **26**, 569), who assigned to it the formula $C_{21}H_{20}O_9$; he hydrolysed it quantitatively, and obtained from it a substance insoluble in water, which he analysed and found to be emodin, and a substance soluble in water which reduced Fehling's solution. He suggests that the latter is the *rhamnodulcite* described by Liebermann, and that the equation for the hydrolysis is $C_{21}H_{20}O_9 + H_2O = C_{15}H_{10}O_5 + C_6H_{12}O_5$. In previous communications one of us, in conjunction with Mr. T. H. Greenall (Trans., 1887, **51**, 52), and subsequently in conjunction with Dr. W. T. Smith (Trans., 1888, **53**, 171), has shown that morindin, the characteristic colouring matter of A'l, the root-bark of *Morinda citrifolia*, also yields on hydrolysis a trihydroxymethylanthraquinone, $C_{15}H_{10}O_5$, which, however, seems not to be identical with emodin. In view, therefore, of the discrepancies in the statements of Faust, of Liebermann and Waldstein, and of Keussler, it became of interest to determine (1) what was the true composition of the frangulin, and what was the real nature of the products of its hydrolysis, and (2), if a trihydroxymethylanthraquinone should turn out to be one product of the hydrolysis, as Liebermann and Waldstein, and also Schwabe assert, whether this body was identical with morindon.

Preparation of Frangulin.

The preparation of frangulin from the bark is a somewhat troublesome and tedious operation, for not only is it present in very small quantities, but it is accompanied by plant fat and resinous substances, from which it is not easily separated. The method we adopted was first to remove the plant fat by repeatedly extracting the crushed bark with low-boiling petroleum, which dissolves very little except the fat and chlorophyll, and then to extract the residue with methylated spirit, the extraction being continued until the liquid running off contained but little colouring matter.

These extractions were performed in an apparatus, Fig. 1, designed on Soxhlet's plan, but modified so as to suit the large quantities of material dealt with. It consisted of a cylindrical tin can, *E*, 10 inches in diameter and 17 inches in height, provided with a removable conical top, *C*, which could be secured to the can by means of a stout brass flange which was pressed by means of a number of clamps to a similar flange attached to the top of the cylinder. A washer cut out of sheet indiarubber and placed between the two flanges kept the apparatus air-tight when the clamps were screwed up. The charge of bark, weighing 14 lbs., was contained in a muslin bag and rested on a false bottom made of thick tin-plate, perforated with holes and supported by legs at a height of about 1½ inches from the bottom of the can. In the side of the can and close to the bottom was a tin tubulure *a*, giving access to the space below the false bottom. Into this, by means of a cork, the end of a tube, *s*, was fitted which rose vertically outside the can to a point a little below the flanges and then bent over and acted as a syphon. To avoid too great rigidity, there was a junction in the tube at *b*. At the top of the conical lid was a tubulure, into which a glass ⊤-piece was fitted. The syphon led to a bottle-shaped copper vessel, *R*, of about four gallons capacity, in which the petroleum or methylated spirit was boiled. The vapour of the solvent was conducted by a wide-bent glass tube, *t*, up to the side branch of the ⊤-piece and through it into a reflux condenser which was joined to the upper extremity *c* of the ⊤-piece. The glass tube *t* was wrapped round with strips of woollen cloth to prevent condensation occurring in it. By employing this apparatus, the same quantity of liquid was made to serve for numerous extractions, as it was syphoned off into the copper can as soon as the tin was full, and was then boiled off again, passed to the condenser, and returned as fresh solvent to the tin. Both the extracting tin and the copper can were surrounded by water-baths and could be heated to suitable temperatures.

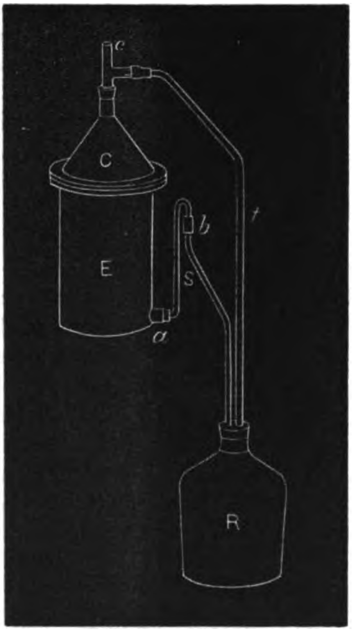


FIG. 1.

The methylated-spirit extract on standing for two days deposited a considerable quantity of dark-brown resinous matter; it was filtered, and to the filtrate a solution of lead acetate in methylated spirit was added in order to remove tannin, the brown precipitate thus produced was filtered off, and through the filtrate a current of sulphuretted hydrogen was passed to throw down the lead present. After separating the lead sulphide by filtration, the solution was put aside for five weeks, and at the end of that time it was found to have deposited some frangulin, which separates from such impure liquids in characteristic little orange-red spheres of some ¼ mm. or so in diameter. This deposit was purified by heating with spirit, which dissolved some brown impurities and was poured off; the residue was then recrystallised from methylated spirit, of which a large quantity was required to effect solution. This preparation, which will be denoted by A for reference, amounted to 2·0 grams and was of an orange-yellow colour.

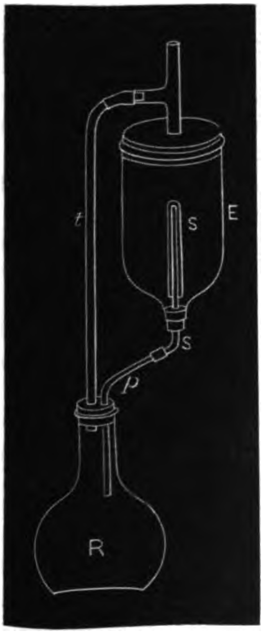


FIG. 2.

The liquid which had deposited the frangulin spheres was next evaporated to dryness with addition of calcium sulphate, which was added in order to get a residue that could be submitted to extraction with ether; it would otherwise have given a brown, pitch-like mass. The residue obtained was further mixed with fragments of pumice to facilitate the extraction, which was performed in a modified form of King's extractor, Fig. 2 (*Chem. News*, 1888, **57**, 235), constructed out of an inverted bell-glass, *E*. This was closed at the bottom by a cork through which a vertical tube, *s*, passed. This tube was ground off at an angle at its upper extremity, and over it was inverted a somewhat wider tube closed at its upper end and reaching nearly but not quite down to the cork at the bottom. A plug of glass wool was placed on the cork, and then the residue mixed with fragments of pumice was packed in, taking care to have a column of pumice fragments round the centre tubes. The wide end of the bell-glass was closed with a large cork through which a glass T-tube passed. This cork was coated with plaster of Paris to prevent escape of ether. The lower end of the tube *s* was bent and passed for a short distance into the end of a slightly wider tube, *p*, and the joint was made good with a piece of indiarubber tubing. The tube *p* led through the cork of a flask, *R*, in which the ether was heated. The vapours of the ether were conducted up a wide tube, *t*, to the side arm of the T-tube, and thence to a reflux condenser connected to the upper end of the T-tube. The condensed ether flowed into the bell-glass, and when it rose above the top of the tube *s*, it was syphoned back into the flask *R* again; thus the operation went on automatically, as in the case of the large extractor.

Some of the extracts obtained deposited fairly pure frangulin; others were so impure that but little frangulin could be got from them. The best extracts were obtained when the amount of calcium sulphate added was sufficient to produce a residue that could be crumbled between the fingers.

The frangulin thus obtained, together with about half a gram obtained in preparing A, but which wanted another purification, was recrystallised from alcohol and gave 2·7 grams (preparation B).

Besides the above two preparations, a little more frangulin was got from the calcium sulphate residue and from various mother-liquors, making the total quantity obtained from 14 lbs. of the bark about 5½ grams, a yield equivalent to 0·09 per cent.

Frangulin is an orange-yellow powder which under the microscope has a crystalline appearance, best seen by reflected light; when in suspension in a liquid, or when a mass has dried in a cake, it often exhibits a silky lustre. It is not very soluble in hot alcohol and is still less soluble in cold, separating as the solution cools; the cold alcoholic solution, however, has a distinctly yellow colour. The presence of a trace of alkali imparts a red tinge to its solutions. It melts at about 225°.

Composition.—The preparations A and B were now analysed; they had been placed over sulphuric acid in a vacuum to dry, and a portion of each was weighed out in a platinum boat and then dried at 120° until the weight became constant.

I. 0·2099 gram of frangulin (preparation A), after drying at 120° until constant, became 0·2061 gram, a loss equivalent to 1·8 per cent., and then on combustion gave 0·4643 gram of CO_2 and 0·0997 gram of H_2O.

II. 0·1884 gram of frangulin (preparation B), after drying at 120° until constant, became 0·1836 gram, a loss equivalent to 2·5 per cent., and then on combustion gave 0·4115 gram of CO_2 and 0·0862 gram of H_2O.

Percentage Composition of Frangulin.

	I.	II.
Preparation	A.	B.
C	61·44	61·13
H	5·37	5·22

The agreement of the analyses of two independent preparations pointed to the substance being homogeneous, and not a mixture, and it will be seen that further analyses confirmed this.

Hydrolysis.

A preliminary experiment showed that when frangulin in solution in methylated spirit was boiled with the addition of aqueous hydrochloric acid, it was decomposed into a substance (which subsequently proved to be emodin) precipitated on diluting with water, and a substance which remained in solution and had the power of reducing Fehling's solution.

Quantitative hydrolyses of preparations A and B were next made. Weighed quantities of A and B were dried at 120° until constant in weight, and then dissolved in alcohol, 10 c.c. of strong aqueous hydrochloric acid added, and the solution boiled for about 3 or 4 hours, using a reflux condenser. After the alcohol had been boiled off until the solution was reduced to a half or a third of its original bulk, it was largely diluted with water, which caused an orange-yellow precipitate to separate; evaporation was continued for some time in order to drive off all alcohol, and the precipitate was collected on a dried and weighed filter paper; it was then washed with water and dried at 120° until constant. The filtrate was almost colourless, and considering the strong tinctorial power of the precipitated substance, practically all of it must have been separated by the treatment adopted.

I. 0·8457 gram of frangulin (preparation A), on drying at 120°

until constant, lost 0·0131 gram (equivalent to 1·55 per cent.). The resulting 0·8326 gram of dry frangulin on hydrolysis gave 0·5710 of product (emodin) insoluble in water.

II. Some frangulin (preparation B), after drying at 120° until constant, weighed 0·7722 gram, and on hydrolysis gave 0·5146 gram of product (emodin) insoluble in water.

Preparation	I. A.	II. B.	Mean.
Yield of product (emodin)	68·6 p. c.	66·6 p. c.	67·6

Product of Hydrolysis insoluble in Water (Emodin).

The product of the hydrolysis thrown down on diluting with water was of an orange colour, and under the microscope proved to be a mass of interlacing needles; it was much more soluble in alcohol than frangulin; with caustic soda solution, it gave a characteristic cherry-red colour.

The products from the hydrolyses of preparations A and B were separately crystallised from alcohol, and combustions were made of them after drying at 120° until constant in weight.

I. 0·2200 gram of the product from the hydrolysis of frangulin (preparation A) after drying at 120° until constant, became 0·2086, a loss equivalent to 5·18 per cent., and then on combustion gave 0·5076 gram of CO_2 and 0·0723 gram of H_2O.

II. 0·1508 gram of the product from the hydrolysis of frangulin (preparation B) after drying at 120° until constant, became 0·1401 gram, a loss equivalent to 7·10 per cent., and then on combustion gave 0·3430 gram of CO_2 and 0·0500 gram of H_2O.

Some more frangulin was hydrolysed in the manner described above, but using a 10 per cent. solution of sulphuric acid in larger volume instead of the hydrochloric acid. The insoluble product obtained was crystallised from benzene, and an attempt was made to sublime it in a vacuum at a temperature of 240°, using a bath of diphenylamine. The sublimate, however, formed too slowly, so the substance was again crystallised from benzene, and used for making two analyses. It was first dried at 180°, but lost nothing by that treatment.

III. 0·2073 gram of the insoluble product, dried at 180°, gave on combustion 0·5000 gram of CO_2 and 0·0701 gram of H_2O.

IV. 0·2003 gram of the insoluble product, dried at 180°, gave on combustion 0·4898 gram of CO_2 and 0·0691 gram of H_2O.

Percentage Composition of the Insoluble Product.

Product from Preparation	I. A.	II. B.	III.	IV.	Mean.	Calculated for Emodin, $C_{15}H_{10}O_5$.
Carbon..........	66·36	66·77	66·91	66·69	66·68	66·67
Hydrogen........	3·85	3·97	3·82	3·83	3·87	3·70
Oxygen..........	—	—	—	—	—	29·63
						100·00

Thus the product of the hydrolysis has the same composition as emodin, as stated by Liebermann and Waldstein, and by Schwabe.

The product obtained from frangulin was compared side by side with some emodin obtained from rhubarb, which Dr. Hugo Müller had kindly furnished, in respect to its colour reactions with strong sulphuric acid and with strong potash solution, and the same cherry-red colours were obtained from both specimens.

Further Analyses of Frangulin.

As the analyses published by Schwabe differed notably from those given on p. 45, we subjected our preparations to further treatment to remove any possible impurities, and then made other combustions, the results of which agreed with those first obtained.

Preparation B was twice recrystallised from alcohol, and then gave the following results:—

III. 0·2133 gram of frangulin, after drying at 120° till constant, lost 0·0045 gram, equivalent to 2·11 per cent.; 0·2081 gram of the frangulin thus dried gave on combustion 0·4669 gram CO_2 and 0·0994 gram H_2O.

IV. 0·2041 gram of frangulin, after drying at 120° until constant, became 0·1997 gram, a loss equivalent to 2·16 per cent., and then on combustion gave 0·4485 gram CO_2 and 0·0950 gram H_2O.

V. 0·2540 gram of frangulin, after drying at 120° until constant, became 0·2485 gram, a loss equivalent to 2·17 per cent., and then on combustion gave 0·5567 gram of CO_2 and 0·1176 gram of water.

Percentage Composition of Frangulin.

(Preparation B twice recrystallised from alcohol.)

	III.	IV.	V.
C	61·19	61·25	61·10
H	5·31	5·29	5·26

Another method of purifying it for analysis was next tried, and still the results proved to be the same as before. Portions of preparations A and B, and of B recrystallised, were mixed and warmed with ether, but not dissolved; filtered and washed with ether; then crystallised from alcohol and washed, first with ether and then with alcohol. Two analyses were made of the frangulin thus prepared.

VI. 0·1543 gram of frangulin, after drying at 120° until constant, lost 0·0033 gram, equivalent to 2·14 per cent. 0·1501 of the frangulin thus dried gave on combustion 0·3366 gram of CO_2 and 0·0721 gram of H_2O.

VII. 0·1998 gram of frangulin, after drying at 120° until constant, lost 0·0055 gram, equivalent to 2·75 per cent. 0·1939 of the frangulin thus dried gave on combustion 0·4348 gram of CO_2 and 0·0920 gram of H_2O.

(Preparations A and B mixed, treated with ether, and recrystallised.)

	VI.	VII.
C	61·16	61·16
H	5·34	5·27

Collecting these analyses together and taking the mean, it will be seen that they are quite concordant, and agree with the formula $C_{22}H_{22}O_9$—

Percentage Composition of Frangulin.

	I.	II.	III.	IV.	V.	VI.	VII.	Mean.	Calculated for $C_{22}H_{22}O_9$.
C ..	61·44	61·13	61·19	61·25	61·10	61·16	61·16	61·20	61·40
H ..	5·37	5·22	5·31	5·29	5·26	5·34	5·27	5·29	5·11
O ..	—	—	—	—	—	—	—	33·51	33·49
								100·00	100·00

Schwabe found, as a mean of five analyses, the figures given below and assigns to frangulin the formula $C_{21}H_{20}O_9$—

	Mean.	Calculated for $C_{21}H_{20}O_9$.
C	60·38	60·57
H	5·32	4·80
O	34·30	34·63
	100·00	100·00

It will be noticed that the mean of Schwabe's analyses differs considerably from that of our analyses. The disparity may perhaps be due to a difference in the way of drying; our frangulin was in every case dried at 120° till constant, losing about 2 per cent. in the process. Schwabe remarks that, on drying, frangulin lost no water of crystallisation, but does not state at what temperature he dried it. If our frangulin had contained $1\frac{1}{2}$ per cent. of water when analysed, the figures would have been carbon 60·28, and hydrogen 5·38, which are very close to those obtained by Schwabe.

The Product of the Hydrolysis Soluble in Water.

In order to determine the nature of the product soluble in water obtained by the hydrolysis of frangulin, the filtrate from the emodin obtained in hydrolysis I was concentrated to a small bulk, and it was heated with the addition of sodium acetate, phenylhydrazine hydrochloride, and water, and evaporated to dryness. The residue was treated with water, when a brown substance remained undissolved, and was collected; this proved to be insoluble in hot water, but dissolved in alcohol; on diluting the alcoholic solution, an orange-yellow precipitate with a brownish tinge separated, this was collected and dried, and its melting point found to be about 158°. Some phenylglucosazone was prepared for comparison, and was found to be quite different from the osazone of the product from frangulin. The product in question is undoubtedly not glucose.

Owing to the small quantities of frangulin hydrolysed, our attempts to isolate the product from the filtrates obtained in the other hydrolyses were unsuccessful.

Conclusions.—The results arrived at are:—

1. That frangulin is a glucoside of the formula $C_{22}H_{22}O_9$, the term glucoside being used in its wider sense as including substances which on hydrolysis yield products capable of reducing Fehling's solution.

2. That the products of its hydrolysis are emodin, identical with the emodin of rhubarb, and a compound which reduces Fehling's solution, but which is not glucose.

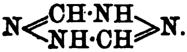
As the yield (67·6 per cent.) of emodin on hydrolysis was higher than the theoretical amount (62·8 per cent.) which $C_{22}H_{22}O_9$ should yield, it was imaginable that the formula was really $C_{21}H_{20}O_9$, and that the higher percentage of carbon obtained was due to the presence of free emodin as an impurity; but this view was discarded, firstly, because the presence of 10 per cent. of free emodin would be required to raise the carbon from 60·58 to 61·20, and this could scarcely be present in each of the four samples that had received different treatment yet gave concordant figures; and, secondly, because the presence of 10 per cent. of emodin would have made the hydrogen 4·70 per cent., an amount differing widely from the 5·29 per cent. obtained.

We are engaged in preparing larger quantities of frangulin with a view of redetermining the yield on hydrolysis and of identifying the soluble product; but as we are unable to continue the investigation together we are now communicating this section to the Society, and the subject will be continued by one of us.

VII.—*The Action of Chloroform and Alcoholic Potash on Hydrazines.*

(Part III.)

By S. Ruhemann, Ph.D., M.A.

It has been previously shown that the action on phenylhydrazine of the agents mentioned in the title gives rise to the formation of a basic substance which is to be regarded as a diphenyl-derivative of *tetrazine*,  $N\begin{smallmatrix}\diagup CH{\cdot}NH \diagdown \\ \diagdown NH{\cdot}CH \diagup\end{smallmatrix}N$. The application of the reaction to homologues of phenylhydrazine has resulted in the formation of homologues of diphenyltetrazine, and it is to the description of several of these compounds that this paper will be devoted.

Paraditolyltetrazine.

In the previous paper (Trans., 1889, 242), although diphenyltetrazine was the chief subject of study, it was mentioned that a ditolyltetrazine could be prepared from paratolylhydrazine. I have subjected this substance to a closer study, and have found that it is a weaker base than diphenyltetrazine, but that, like the latter, it dissolves, although with difficulty, in boiling hydrochloric acid, from which, on cooling, slender, white needles of the hydrochloride are deposited. These are, however, very unstable, and, on drying over potash and sulphuric acid, continually lose hydrogen chloride. This circumstance explains the discrepancy which will be observed in the following numbers:—

	Calculated for $C_{16}H_{16}N_4,HCl$.	Found. I.	Found. II.
Cl	11·81	10·76	11·0

Paraditolyltetrazine combines with 1 mol. of methyl iodide, when it is heated with a solution of the iodide in methyl alcohol at a temperature of 100°, and yields a *methiodide* of the formula $C_{16}H_{16}N_4,CH_3I$, as shown by the analysis :—

	Calculated.	Found.
I	31·28	31·16
N	13·793	14·00

This compound is sparingly soluble in boiling water, and crystallises from the aqueous solution in colourless needles which melt at 242°.

Nitroparaditolyltetrazine is formed by adding fuming nitric acid to the solution of the tetrazine in acetic acid, and is thrown down by water as a yellow precipitate which is easily soluble in glacial acetic acid and in alcohol, and crystallises from methylated spirit in orange needles which melt at 144°.

The formula, $C_{16}H_{15}(NO_2)N_4$, requires—

		Found.	
	Theory.	I.	II.
C	62·14	62·5	—
H..........	4·85	5·0	—
N..........	22·65	—	22·75

The formation of a nitro-compound, so readily soluble in acetic acid and with such a low melting point as compared with that of nitrodiphenyltetrazine (above 300°), led me to repeat this experiment; but I arrived at the same result. There is only one nitro-derivative formed.

I, therefore, reinvestigated the action of nitric acid on diphenyltetrazine, and found that besides the nitro-derivative already described, there is formed another which is easily soluble in acetic acid or alcohol, and crystallises from the latter in yellowish-red needles which melt at 145—146°. A nitrogen determination proved this substance to be an isomeric *nitrodiphenyltetrazine.* The formula, $C_{14}H_{11}(NO_2)N_4$, requires :—

	Theory.	Found.
N	24·91	24·98

The action of bromine on paraditolyltetrazine results in the formation of two bromine-derivatives. On adding bromine to the solution of the tetrazine in glacial acetic acid, a white, crystalline precipitate separates which, when recrystallised from the same solvent or from boiling alcohol, forms needles melting at 245° with decomposition. A nitrogen determination of this substance proved it to be a *dibromoparaditolyltetrazine.* Its formula, $C_{16}H_{14}Br_2N_4$, requires—

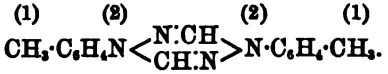
	Theory.	Found.
N	13·27	13·67

Besides this bromine-derivative, another is also formed, which remains dissolved in the acetic acid after the first has separated out, but can be precipitated from it by water. It is extremely soluble in alcohol, and crystallises from dilute spirit in colourless, slender needles which melt at 81°. Lack of material prevented me from analysing this substance; but from analogy to the action of bromine on diphenyltetrazine, it is probable that the compound melting at 81° is an isomeric dibrominated substitution-product.

Orthoditotyltetrazine.

This is prepared by a method similar to that which yields the other tetrazines; but in this case it is necessary to take the precaution of adding the alcoholic potash to the solution of the hydrazine and chloroform in spirit very gradually; warming only slightly until the reaction begins, or else the hydrazine suffers complete decomposition, and a brown, viscid mass is formed. The product of the reaction was treated as in the other cases, namely, after dilution with water it was shaken with ether, the unaltered hydrazine removed from the ethereal solution by dilute sulphuric acid, and the ether evaporated. A brown oil was then left, and from this, after some time, crystals separated; these are readily soluble in alcohol, and crystallise from it in slightly coloured plates. This substance is *orthoditolyltetrazine*. For complete purification, it was found advisable to transform it into the hydrochloride and to decompose this by boiling with an aqueous solution of ammonia. The tetrazine is thus obtained in colourless crystals which melt at 141°.

The following numbers correspond with the formula—



$$\overset{(1)}{CH_3}\cdot\overset{(2)}{C_6H_4}N<\begin{matrix}N:CH\\CH:N\end{matrix}>\overset{(2)}{N}\cdot C_6H_4\cdot\overset{(1)}{CH_3}.$$

	Theory for $C_{16}H_{16}N_4$.	Found. I.	Found. II.
C	72·73	72·704	—
H	6·06	6·09	—
N	21·21	—	21·32

This formula was, moreover, verified by the determination of the molecular weight, and by the study of its behaviour towards nitric and sulphuric acids.

A molecular-weight determination by Raoult's method gave the following result:—

Weight of substance	0·4104 grams.
„ acetic acid	23·9212 „
Freezing point of acetic acid....	14·60° C.
„ mixture......	14·86 „
Depression of freezing point	0·26 „
Molecular weight derived from the above data	258
Theory for $C_{16}H_{16}N_4$............	264

Orthoditolyltetrazine is dissolved by boiling hydrochloric acid, and the solution on cooling deposits white needles of the *hydrochloride* which, when dried at 100°, lose hydrogen chloride, but may be dried over sulphuric acid and potash without suffering decomposition—as shown by the analysis, which gave:—

	Calculated for $C_{16}H_{16}N_4,HCl$.	Found.
Cl	11·81	11·61
N	18·64	18·77

Orthoditolyltetrazine also combines with 1 mol. of methyl iodide when the two are heated together in methyl alcohol solution at 100° for a few hours. If the solution is evaporated on the water-bath and the residue dissolved in boiling water, white nodules crystallise out on cooling: these melt at 198° and turn slightly yellow on drying at 100°.

The following numbers correspond to the formula $C_{16}H_{16}N_4,CH_3I$:—

	Theory for $C_{17}H_{19}N_4I$.	Found.
N...........	13·79	13·93
I	31·28	30·74

The action of sulphuric acid on orthoditolyltetrazine gives rise to a *sulphonic acid;* this is obtained on warming the base with concentrated sulphuric acid, when it dissolves. On adding water, a slightly bluish precipitate is thrown down, which is sparingly soluble in boiling water, and on cooling crystallises in colourless prisms which are free from water of crystallisation, and gave on analysis values corresponding to the formula $C_{16}H_{15}N_4{\cdot}HSO_3$:—

	Theory.	Found.
S	9·3	9·15
N...........	16·28	16·56

On adding fuming nitric acid to the solution of the tetrazine in glacial acetic acid, crystals are deposited after a short time which are sparingly soluble in alcohol, and crystallise from it in yellow needles melting at 206—207°.

Analysis shows this compound to be a *mononitro-derivative* of orthoditolyltetrazine. The formula, $C_{16}H_{15}(NO_2)N_4$, requires—

	Calculated for $C_{16}H_{15}N_5O_2$.	Found. I.	Found. II.
C........	62·13	61·873	—
H........	4·85	4·91	—
N........	22·65	—	22·80

Whilst the formation of tetrazines from phenylhydrazine and paratolylhydrazine is accompanied by that of the formyl-derivatives of the corresponding hydrazines, formylorthotolylhydrazine could not be obtained by the isonitrile reaction; it is, however, easily prepared by heating orthotolylhydrazine with formamide in an oil-bath at about 120° until ammonia ceases to be evolved. The product of the reaction solidifies on cooling and crystallises from water in colourless plates melting at 120°; these on analysis gave numbers corresponding to the formula $CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH{\cdot}CHO$ [$CH_3 : NH = 1 : 2$]:—

	Calculated for $C_8H_{10}N_2O$.	Found. I.	Found. II.	Found. III.
C	64·0	64·2	—	—
H	6·67	6·87	—	—
N	18·67	—	18·53	18·80

Although the preceding researches are in themselves sufficient to show that in general the action of chloroform and alcoholic potash on phenylhydrazine and its homologues gives rise to substituted tetrazines, yet I thought it desirable to apply this reaction to a still higher member of the primary hydrazines. I have chosen pseudocumylhydrazine.

Pseudocumylhydrazine.

This compound has already been obtained by Haller (*Berichte*, **18**, 89) by the method described by E. Fischer (*Annalen*, **190**, 67) for the preparation of phenylhydrazine. I can confirm Haller's statement that pseudocumylhydrazine cannot be prepared according to V. Meyer and Lecco's method (*Berichte*, **16**, 2976), as on mixing the stannous chloride and diazo-solution evolution of nitrogen takes place, and a tarry product is formed.

Pseudocumylhydrazine is sparingly soluble in ether and decomposes readily. Before applying the isonitrile reaction to this base I have subjected it to a closer study with the object of characterising it by some derivatives.

Acetylpseudocumylhydrazine.—Acetic anhydride acts on the hydrazine with development of heat. The reaction was completed on the water-bath and the product recrystallised from boiling water. It forms colourless plates which are readily soluble in alcohol and melt at 156—157°. When submitted to analysis, it gave numbers corresponding to the formula $C_6H_2(CH_3)_3{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}CH_3$:—

	Theory for $C_{11}H_{16}N_2O$.	Found. I.	Found. II.
C	68·75	68·57	—
H	8·33	8·41	—
N	14·57	—	14·60

Pseudocumylsemicarbazide is formed by adding an aqueous solution of potassium cyanate to a solution of the hydrazine hydrochloride in water. The precipitate thrown down is sparingly soluble in water, but readily in alcohol, and crystallises from the latter solvent in colourless needles which melt at 195°.

The formula, $C_6H_2(CH_3)_3{\cdot}NH{\cdot}NH{\cdot}CO{\cdot}NH_2$, requires:—

	Theory for $C_{10}H_{15}N_3O$.	Found. I.	Found. II.
C	62·17	61·93	—
H	7·77	7·78	—
N	21·76	—	21·97

Benzylidene-pseudocumylhydrazine, $C_6H_2(CH_3)_3{\cdot}NH{\cdot}N{:}CH{\cdot}C_6H_5$, prepared from the hydrochloride of the hydrazine in the usual manner, crystallises from alcohol in coloured needles which decompose at 100° and also, after some time, at the ordinary temperature.

A nitrogen determination of this substance dried in a vacuum over sulphuric acid gave—

	Calculated for $C_{16}H_{18}N_2$.	Found.
N	11·76	12·0

Pseudocumylhydrazine-pyruvic acid,

$$C_6H_2(CH_3)_3NH{\cdot}N{:}C(CH_3){\cdot}COOH.$$

On adding pyruvic acid to an aqueous solution of the hydrazine hydrochloride, a lemon-yellow, flocculent precipitate is at once thrown down which is soluble in alcohol and crystallises from it in yellow needles melting at 148° with decomposition.

The formula, $C_{12}H_{16}N_2O_2$, requires—

	Theory.	Found. I.	II.	III.
C........	65·45	65·20	—	—
H........	7·27	7·36	—	—
N........	12·73	—	12·69	12·97

Pseudocumylhydrazine, when treated with chloroform and alcoholic potash in the manner previously described, yields a compound which is very sparingly soluble in alcohol but readily in boiling glacial acetic acid, and crystallises from the latter in yellow needles which melt at 234°. This substance is, without doubt, *dipseudocumyltetrazine*.

I hope to communicate to the Society the results of the further study of this tetrazine in another paper.

I may here mention that I have already begun to study the action of chloroform and alcoholic potash on other derivatives of phenylhydrazine. In a note published recently in conjunction with F. F. Blackman (Trans., 1889, 612) it was stated that the above-mentioned reagents do not yield the corresponding tetrazine with benzophenylhydrazine. I have since then applied the isonitrile reaction to parabromphenylhydrazine. When this hydrazine, which has been described by Neufeld (*Annalen*, **248**, 94), is treated with alcoholic potash and chloroform it yields, after removal of the unaltered hydrazine, a crystalline residue. Hot water extracts from it a substance which, when repeatedly recrystallised from boiling water, can be obtained in colourless, irridescent needles melting at 198°. Analysis of this compound proved it to be formyl-parabromophenylhydrazine.

Its formula, $C_6H_4Br\cdot NH\cdot NH\cdot CHO$ [Br : NH = 1 : 4], requires:—

	Theory for $C_7H_7N_2OBr$.	Found. I.	II.	III.
N........	13·02	13·44	13·19	—
Br.......	37·2	—	—	37·12

The formyl-compound is the chief product of the isonitrile reaction on parabromophenylhydrazine, but along with it a substance is formed which decomposes so readily that hitherto I have been prevented from analysing it. I shall, however, repeat this experiment, and hope to lay the result before the Society in my next communication.

University Laboratory,
Cambridge.

VIII.—*Note on the Identity of Cerebrose and Galactose.*

By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, PhD., F.I.C.

IN a recent number of the *Zeitschrift für physiologische Chemie* there is a paper by H. Thierfelder, showing the identity of the brain-sugar, *cerebrose*, with the well-known carbohydrate, *galactose* (*Zeit. physiol. Chem.*, **14**, 209). Cerebrose was first described by Thudichum (see *Annals of Chem. Medicine*, **2**, 209; also *Treatise on the Chemical Constitution of the Brain*, p. 143), who found it amongst the products of the long continued action of dilute sulphuric acid at 130° upon certain nitrogenised constituents of the brain.

It is a crystallisable sugar, resembling milk-sugar in its feebly sweet taste and in the great hardness of its crystals, and it is described by its discoverer as having a cupric reducing power equal to about five-sixths of that of dextrose, and as giving in the polariser a "limited rotation" of $+70° \ 40'$. On analysis, numbers were obtained consistent with a formula of $C_6H_{12}O_6$.

The cerebrose which was employed by Thierfelder (*loc. cit.*) was obtained from *cerebrin* by the action of dilute sulphuric acid at high temperatures. It was found, on oxidation with nitric acid, to yield mucic acid, just as does galactose; and in its melting point, specific rotatory power, and cupric reducing power, gave numbers so closely in accord with those obtained with galactose, that there can be no doubt as to the identity of the two sugars.

In the early part of last year (1888), whilst we were engaged on the determination of the molecular weights of the carbohydrates by Raoult's freezing method, Dr. Thudichum was good enough to place in our hands for examination a specimen of cerebrose, which he had prepared some years previously from pure *phrenosin*. We made a careful examination of its properties, and proved to our complete satisfaction that it was *galactose*. Although we have but few new facts to add to the very complete work of Thierfelder, it seems worth while to place on record the independent proof of the identity of the two sugars, especially as the specimen we have examined is the one described by Thudichum in his first notice of cerebrose.

Specific Rotatory Power.

(5·6198 grams *cerebrose* per 100 c.c.)

(1) $[\alpha]_j \ 87{\cdot}46° = [\alpha]_D \ 78{\cdot}93°$ at 18° C.

(2) $[\alpha]_j \ 86{\cdot}78 \ = [\alpha]_D \ 78{\cdot}32$ at 21° ,,

Specific Rotatory Power of galactose.

$[\alpha]_D$ 80·56° at 18° C.
$[\alpha]_D$ 79·93 at 21 „

Cupric Reducing Power.

(Strength of solution, 5·6198 grams cerebrose per 100 c.c.)

(1) 0·1124 gram *cerebrose* reduced .. 0·24145 gram CuO.
(2) 0·1686 „ „ .. 0·36273 „

(1) $\kappa = 97{\cdot}42$
(2) $\kappa = 97{\cdot}57$
Galactose $\kappa = 93{\cdot}01$

The cerebrose used in the above determinations was not recrystallised by us, and the slight divergence of the above numbers from those of galactose is probably accounted for by the presence of a little *dextrose*, which, from an examination of the uncrystallisable mother-liquor (also handed to us by Dr. Thudichum), we have reason to believe is formed in the hydrolysis of phrenosin together with the cerebrose.

We have prepared the phenylhydrazine-compounds of cerebrose and of galactose under identical conditions, and find their melting points as follows:—

Phenylcerebrosazon, m. p. 142°
Phenylgalactosazon, m. p. 146

Thierfelder found a much higher melting point than the above, but this is probably accounted for by the fact that galactose yields, just as some of the other sugars do, several compounds of this nature. Our results agree in this important point, that when treated under similar conditions cerebrose and galactose yield phenylhydrazine-compounds having identical melting points.

Molecular Weight of Cerebrose determined by Raoult's Freezing Method.

Freezing point of water used, 0·085°.
Strength of solution, 5·6198 grams *cerebrose* in 96·58 grams water.

E.	C.	A.	M.
−0·570	0·655	0·112	170
−0·570	0·655	0·112	170

	Calculated for $C_6H_{12}O_6$.	Found.
A	0·106	0·112
M	180·0	170·0

A comparison of the microscopical appearance of the crystals of cerebrose and of galactose indicates beyond doubt the identity of crystalline habit.

IX.—*Arabinon, the Saccharon of Arabinose.*

By C. O'Sullivan, F.R.S.

Amongst the products of the action of sulphuric acid on arabic acid (Trans., 1884, **45**, 55), I indicated the presence of a compound which I named α-arabinose, and of which I said "the optical activity must be well above $[\alpha]_j = 140°$." Whilst working with the dextro-rotatory gums (Gedda gum), I frequently noticed that the sugar syrups had a higher optical activity than arabinose, the β-arabinose of the above paper, thus indicating the presence of a substance of high rotatory power. It often happened, however, that there was little or no evidence of the presence of this compound, and this frequently under conditions such as I thought warranted me to expect it in greatest quantity. There were here, then, evidently some circumstances, a knowledge of which could only, if at all, be arrived at by a study of the substance itself.

A 25 per cent. solution of *geddic acid* (an acid obtained from Gedda gum, which I shall describe in a future communication) was heated to boiling, and 2 per cent. of sulphuric acid added, this having previously been diluted with 4 or 5 volumes of water. At the end of 15 minutes' digestion the solution was cooled, and alcohol, sp. gr. 0·830, added as long as a precipitate was thrown down. When the supernatant liquid became clear, it was decanted off and the acid neutralised with strong baryta-water. The sulphate and other salts of barium were filtered off and the alcoholic liquid evaporated to a syrup in a vacuum; from this, arabinose crystallised out, and a further crop was obtained from the mother-liquor by the addition of a little dry methyl alcohol.

Ethyl alcohol, sp. gr. 0·820, was added to the methylic mother liquor until a slight precipitate formed; this contained a trace of barium, and if sufficient alcohol had been added and the original syrup was sufficiently free from water, the alcoholic solution would be fairly free from that metal. The clear alcoholic liquid was decanted off and ether added as long as a precipitate formed. An examination of this syrupy precipitate showed that it did not contain barium, and that it was not acid, demonstrating the absence of a gum acid; and that the solid matter it contained had an optical activity of $[\alpha]_D = 163°$. This syrup was dissolved in a little methyl alcohol and allowed to stand for some months; the solution showed no signs of crystallisation; hence I determined to make such an examination of the substance as was possible under the circumstance.

Ethyl alcohol, sp. gr. 0·820, was added to the methylic solution; a large, syrupy precipitate was first formed, but further addition of the solvent partly redissolved it; the precipitate was allowed to settle and the clear supernatant liquid poured off. This precipitate is fraction *a*. Ether was added to the clear liquid until a quantity of precipitate was obtained, estimated as one-third of the whole matter in solution; this was allowed to settle, it is fraction *b*. A further addition of ether to the clear supernatant liquid yielded another precipitate, fraction *c*. The optical activity of these three fractions was determined with the following results:—

Fraction *a* gave $[\alpha]_D = 187·2$
" *b* " $[\alpha]_D = 188·9$
" *c* " $[\alpha]_D = 187·6$

Hence, a large quantity of a substance of lower rotating power was eliminated, and we have in these three fractions the compound in a state of moderate purity. A determination of the cupric reducing power was made. 2·261 grams of solution of a sp. gr. 1·01426 gave 0·113 gram CuO; from this K = 62·1. The quantity of substance in solution in this case and in the determination of the specific rotatory power was estimated on the supposition that 10 grams of the substance in 100 c.c. of solution gives a sp. gr. of 1·0385. The true factor will have to be determined later.

The three fractions were again mixed, and the solution evaporated in a vacuum to a syrup. This was taken up with methyl alcohol, a small fraction taken out by adding strong ethyl alcohol, and then ether added as long as a precipitate formed. The optical activity of the solid matter in this syrup, determined as above, was found to be $[\alpha]_D = 192·5$. A further quantity of low rotating substance was therefore eliminated by this fractional precipitation. No trace of crystallisation appeared in this syrup or in its solution in dry methyl alcohol after standing for some weeks. I had, therefore, to try to further purify the substance by fractional precipitation after the manner already described. Proceeding in this way, I at last obtained a fraction, of which the specific rotatory power was $[\alpha]_D = 196·7$, with a $\kappa = 57·3$. Considering the number of fractionations and the slow increase of optical activity and slight diminution in copper oxide reducing power, this fraction may be looked upon as a pure compound, as pure as, indeed, it is possible to get it in the absence of crystallisation. We may therefore safely proceed to the closer examination of its characters and properties.

The syrup was dried in a vacuum over sulphuric acid, and then at a temperature gradually increasing to 75—80° until the weight became constant. In this way a fused, glassy mass was obtained, which, on cooling, solidified to a brittle glass. On pulverisation, this yielded a white, highly hygroscopic powder. A portion of the powder was taken and again gradually dried at 55° in a current of dry air under a pressure of 165—200 mm. of mercury. When the temperature was raised to 70—75°, the substance fused. The weight became constant at 55° at the pressure and under the circumstances indicated. 2·594 grams of dry substance gave 100 c.c. of solution of sp. gr. 1·01022, and this solution, in a 200 mm. tube, had an optical activity $\alpha_D = + 10·3°$. From these observations we find that a solution containing 1 gram dry substance in 100 c.c. has a sp. gr. of 1·00394—reasoning from analogy, the amount of this substance in any solution, up to a sp. gr. of 1·04500 at least, can be calculated with practical accuracy by employing this factor—and that the specific rotatory power of the compound is $[\alpha]_D = + 198·5°$. 3·203 grams of a solution sp. gr. 1·02554 yielded on usual treatment 0·262 gram CuO; hence the cupric reducing power, or κ is 58·8, that is, 100 parts of it reduce as much copper as 58·8 parts of dextrose.

4·938 grams of dry substance were digested at 100° for 30 minutes with 20 c.c. of 2 per cent. sulphuric acid. The acid was separated with baryta-water, and the filtrate from the barium sulphate made up to 100 c.c. with the washings; in testing for neutralisation, there was, of course, some slight loss. The solution had a sp. gr. of 1·01995, and in a 200 mm. tube gave $\alpha_D = + 11·25°$. From this the solid matter has a specific rotatory power $[\alpha]_D = + 108·6°$, a number closely agreeing with that of arabinose. It was evaporated to a syrup; on standing, this solidified to a mass of sphenoidal crystals, highly characteristic of that body, crystallising under like conditions. These were washed with as little methyl alcohol as possible, the washings yielded a further crop of crystals, and the mother liquor from these again crystallised on evaporation to a syrup. Over 70 per cent. of the material taken was obtained in the two crops of crystals. Both crops were mixed, as the crystals were identical, and a solution was made of them containing in 100 c.c. 4·97 grams of dry substance; the optical activity of this was found to be $\alpha_D = + 10·52°$ in a 200 mm. tube, its sp. gr. 1·01914, and 1·897 grams of it reduced 0·221 gram CuO. From these numbers we have 1·00385 as the sp. gr. of a solution containing 1 gram in 100 c.c., $[\alpha]_D = 105·8$ as its specific rotatory power, and its $\kappa = 108·3$.

These are practically the factors of pure arabinose; hence the compound acted on by sulphuric acid holds the same relation to arabinose as does either dextrin (amylin) or maltose (amylon) to dextrose (amylose). Is it an "*in*" compound or an "*on*" one? Arabinose has recently been satisfactorily proved to be $C_6H_{10}O_5$; if the substance with which we are dealing is an "*on*" compound, its molecule is $C_{10}H_{18}O_9(2C_6H_{10}O_5-H_2O)$, if an "*in*" one it is $nC_5H_8O_4$, n being considerably greater than 2. Raoult's method of determining molecular weights seemed to be a simple and an expeditious way of determining the question. The freezing point of a solution of the substance, sp. gr. 1·02554, and consequently containing 6·466 grams of the dry substance in 100 c.c., was 0·535° below that of water; thence, by Raoult's law, $19 \div \frac{96{\cdot}088 \times {\cdot}535}{6{\cdot}466 \times 100} = 239{\cdot}2$, the molecular weight of the substance. The molecular weight of $C_{10}H_{18}O_9$ is 282; hence, although the number obtained is low, when we consider that the molecular weight of some of the "*on*" compounds comes out low by Raoult's method (Brown and Morris, Trans., 1888, **53**, 615; Tollens and Mayer, *Ber.*, **21**, 1566), and that the preparation may not be absolutely free from ash, which we know materially affects the results, we have sufficient evidence, that the compound belongs to the "*on*" and not to the "*in*" class. The new substance is then $C_{10}H_{18}O_9$, the saccharon of arabinose. I, therefore, propose to call it *arabinon:* according to the nomenclature proposed by Scheibler (*Ber.*, **18**, 646), the compound would be *arabinbiose.* I prefer the vowel nomenclature, and, therefore, the term I propose.

A $C_{12}H_{22}O_{11}$ sugar requires—

C	42·11 per cent.
H	6·43 „

And a $C_{10}H_{18}O_9$ compound—

C	42·58 per cent.
H	6·38 „

The difference in percentage of carbon is sufficiently great to be apparent on determination. A combustion of arabinon was made, in a current of oxygen, side by side with one of saccharon (cane-sugar), in a like time and under similar conditions, with the following results:—

Dry saccharon employed, 0·3329 gram; found CO_2 = 0·514 gram, H_2O = 0·198 gram.

Dry arabinon employed, 0·3495 gram; found CO_2 = 0·541 gram, H_2O = 0·205 gram and ash = 0·002 gram.

These numbers correspond to—

	Saccharon.	Arabinon.
C	42·11 p. c.	42·46 p. c.
H	6·61 „	6·55 „

There can, therefore, be no doubt that the formula of arabinon is $C_{10}H_{18}O_9$.

If we now turn to the results obtained above by acting on arabinon with sulphuric acid, we find that the observed increase due to the hydrolysis is 4·9 per cent., or 100 parts arabinon yielded 104·9 parts arabinose. The equation

$$\underset{\text{Arabinon.}}{C_{10}H_{18}O_9} + H_2O = \underset{\text{Arabinose.}}{2C_5H_{10}O_5}$$

requires 106·3 parts arabinose, a number sufficiently close to that observed, when we consider that the operations could not be performed without some loss, to confirm the conclusion as to the nature of the compound. We have, therefore, in the new compound, arabinon, a sugar holding the same relation to arabinose that maltose dose to dextrose. I have not yet succeeded in crystallising it. In the syrupy state, it dissolves easily in dry methyl alcohol; from this, strong ethyl alcohol, of sp. gr. 0·820, precipitates it partially, and an excess dissolves it. Ether throws it out of this solution almost completely. The highest specific rotatory power observed is $[\alpha]_D = +202°$ (C = 6·466). There is apparently an increase with the concentration. Its κ is not greater than 58. If it be considered that 2 mols. of arabinon reduce 9 mols. CuO, the κ would be 57·5, and the sp. gr. of a solution containing 10 grams dry substance in 100 c.c. is 1·0395. To the taste it is distinctly sweet, and in that respect it is sharp and clean like saccharon. It is easily diffusible through parchment paper; sulphuric acid readily hydrolyses it to arabinose. This inversion clearly explains the irregular absence and presence of the compound of high rotatory power amongst the sugar syrups obtained by the action of sulphuric acid on the gums, and points out the direction to be followed in order to prepare it in quantity.

I have demonstrated the presence of arabinon in the syrups obtained by the modified action of sulphuric acid on arabic acid, the chief gum acid of all the lævorotatory gums I have hitherto examined, such as gum arabic, Turkey, Senari, Levantine, and East India gums, and on the acids obtained from two varieties of dextrorotatory gum (Gedda gum).

In the immediate future I hope to further add to our knowledge of arabinon, and I shall be disappointed if I do not succeed in crystallising it.

Much of the analytical work in this paper, and of the general work that led to the results, was done by my assistant, Mr. A. L. Stern, B.Sc. My cordial thanks are due to him.

X.—*The Nature of Solutions, as elucidated by a Study of the Density, Electric Conductivity, Heat Capacity, Heat of Dissolution, and Expansion by Heat of Sulphuric Acid Solutions.*

By Spencer Umfreville Pickering, M.A.

TABLE OF CONTENTS.

PAGE
Part I. *General and Introductory* 65
 Origin and nature of the work 65
 Methods of differentiation employed 67

Part II. *Densities* 69
 Method employed 69
 Experimental error 70
 Temperature of the determinations 71
 Preparation of the solutions 72
 Results obtained 73
 Second differentiation 76
 Position of the changes of curvature 77
 Conclusions drawn from the densities 78
 Mendeléeff's views 79
 Contraction on mixing 79
 Construction of a density table 84

Part III. *Electric Conductivity* 86

Part IV. *Heat Capacity* 88
 Method employed 89
 Experimental error 90
 Results obtained 90

Part V. *Heat of Dissolution* 94
 Discussion of Berthelot's and Thomsen's results 94
 Graphic representation of results 97
 Methods employed 98
 Calculation of results 98
 Experimental error 100
 Results obtained 101
 "Dissolution" experiments 101
 Effects of excessive smoothing of the curve 104
 Direct differentiation 104
 "Mixing" experiments 105
 Position of the changes of curvature 108
 Comparison with Pfaundler's and Thomsen's results 109

Part VI. *Expansion by Heat* 114
 A. As a function of percentage composition 114
  Results 115

PAGE
Differentiation of the results 116
Position of the changes of curvature 117
Position of maxima 119
B. As a function of temperature 119
Regularity shown by the cases specially investigated 120
Irregularity shown in other cases 121

PART VII. *Discussion of the Results* 122
The method of analysing the results and curves 122
Experimental error 123
Multiplicity of the changes of curvature 124
Specific changes of curvature as distinct from general changes of direction 125
Agreement of the results from different sources 125
Definite composition of the hydrates indicated 128
Discovery of the extreme hydrates 128
Possible relationship between some of the hydrates 129
Complexity of the highest hydrates 129
Apparent magnitude of the changes at the extreme ends of the figures 130
Indication of the monohydrate in solution 130
Nature of the curves 132
The first differential is probably never rectilineal 132
The second differential probably is so 132
Limits of differentiation 133
Different nature of the curves representing different properties 134
Influence of temperature on the hydrates in solution 1 4
Summary 1 5
Conclusion 137

TABLES I to XXIV 139
PLATES 1 to 3 184

PART I.—GENERAL AND INTRODUCTORY.

IN the early part of 1887, I began an investigation on the nature of solutions, by making a number of determinations of the heat of dissolution of solutions of calcium chloride and nitrate, with the view to settling whether the curves representing these results exhibited any sudden changes indicative of the existence of liquid hydrates, or not. The subsequent publication of Mendeléeff's examination of the densities of alcohol (Trans., 1887, 778) and sulphuric acid (*Zeit. physikal. Chem.*, 1, 275), and of Crompton's examination of F. and W. Kohlrausch's determinations of the electric conductivity of solutions of the latter substance (Trans., 1888, 116), showed that sudden alterations in curvature might be established more satisfactorily by plotting out the rate of change—that is, the first differential coefficient—than by a mere inspection of the original curve, or by attempting to apply equations to it. Mendeléeff stated that the rate of change of the densities is represented by a series of straight lines, meeting at points corresponding with hydrates of definite molecular composition, whilst Crompton found that, in the case of the electrical conductivities, two differentiations had to be applied before a rectilineal figure was obtained. These results are tantamount to the densities, s, of p per cent. solutions being represented by a series of different parabolas of the form $s = A + Bp + Cp^2$, while the conductivities, k, are represented by a series of the form of $k = A + Bp + Cp^2 + Dp^3$, any one equation holding good between two definite hydrates. Crompton's results added confirmation to the particular hydrates indicated by Mendeléeff.

On examining by differentiation my results with the heat of dissolution of the calcium salts, I found that they yielded rectilineal figures only after a double application of the process, and the hydrates thereby indicated were very numerous; further confirmation of these hydrates was obtained by determining the densities of the solutions, which were found, in accordance with Mendeléeff's statement, to yield a series of straight lines after the first differentiation (see Proc., 1888, 35).

These cases, however, were so complicated that I proceeded to investigate the presumably simpler case of sulphuric acid. The nature of the heat of dissolution curve was found to be the same as in the case of the calcium salts, but the hydrates thereby indicated were far more numerous than those which Mendeléeff had mentioned, and, on examining his density results more closely, I found, with surprise, that the values which he quoted* by no means warranted the conclusion that the first differential consisted of straight lines. These values appeared to me to be too meagre to settle the question at issue, so I made a series of fresh determinations, repeating them at four different temperatures. The results confirmed the existence of those hydrates which the heat of dissolution had indicated, and showed that the curves required a second differentiation before they yielded a rectilineal figure.

From these densities the expansion by heat was deduced, and further confirmation of the hydrates thus obtained. The heat capacities of the weak solutions had also been determined in order to calculate out the heat of dissolution results, and these also afforded similar evidence of an independent nature.

The present communication is confined to the results with sulphuric acid.

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* Not determined by Mendeléeff himself, but collected by him from various sources.

Methods of Differentiation employed.

The results obtained, and generally also the curves representing them, were examined by the same process of differentiation as that adopted by Mendeléeff.

When the difference between the densities, &c., of two solutions is divided by the difference in the percentage composition of these solutions, the value obtained gives the mean rate of change in the densities between the two percentages taken, or, as it has to be less perfectly expressed, the mean rate at a point intermediate between these percentages. This constitutes direct differentiation from the experimental values themselves.

Differentiation, however, is a very dangerous and, at the best, a very imperfect tool. The differential is, strictly, the tangent of a curve, and the method here adopted assumes that the curve, which would represent the results, is a straight line between every two experimental points. The method would yield absolutely true results only if these differences were infinitely small; whereas if they be reduced too much—generally below 1 per cent.—the experimental errors attain such relatively large proportions that the results are useless.

The actual differences between the experiments will also affect the form of the differential to a certain extent, and irregularities will be caused if the differences are not the same throughout.

When the experiments themselves form a curved figure consisting of a series of different curves, they will, when differentiated, yield a series of other curves or straight lines, between each of which there will generally be one differential point conforming with neither of the adjacent curves, it being derived from two experiments belonging to two different primary curves. The existence of an undoubtedly non-conformable point is strong proof of a change in the vicinity,* but, when doubtful, it only adds to the difficulty of interpreting the results.

When a second differentiation has to be performed, it is hardly ever possible to apply it to the experimental values themselves, as Crompton did in the case of the conductivities, for the quantities dealt with would be of about the same magnitude as the experimental errors themselves. In such cases we must diminish the error by drawing a smoothed curve through the first differential points, taking readings from this curve and differentiating these. Except in the case of the densities,† I have performed the first differentiation on the smoothed curve representing the experiments, as well as on the experimental values themselves.

---

* Any error in an experiment will affect the two differential points derived from it, in opposite directions.

† To plot the densities out so as to allow 0·0001 gram to 0·01 inch, the whole curve would have to measure about 2000 inches, a wholly impracticable length.

In differentiating the smoothed curve, we have the advantage of being able to take as many points as we like, and at equal distances apart; but, on the other hand, the drawing being subject to the "taste" of the draughtsman, it is never safe to dispense entirely with direct differentiation, especially as changes in curvature will be less marked in the original curve than in the first differential figure, and may be overlooked, if we trust entirely to the former. It requires no little practice, and the most careful attention to the magnitude of the experimental errors, to draw the smoothed curve on which to perform the differentiation. The curves representing the present results have been drawn with the help of a long thin steel or wooden lath. Such a lath, when bent under the four points of pressure exerted by one's two hands, does not form a curve of any particular nature, and does not necessarily give a curve which will differentiate eventually into a straight line; but I find that if the experiments form a figure on to which the bent steel *cannot* be fitted, that figure certainly does *not* consist of a single parabolic curve.*

The scale which I have used, wherever practicable, is such that the experimental error is represented by one-tenth to one-twentieth of the distance between the points, the maximum error corresponding to about one-tenth of an inch. Readings from these curves were taken with an accuracy of one-hundredth of an inch or less. Drawings on several different scales, and with several different points as origins, were made in all cases, and the labour entailed in the treatment of the results has by far exceeded that of the determinations themselves.

In cases where the experimental error was comparatively large, the results have been divided into two independent series, and each of these differentiated separately; the results being then plotted out together. In such a case it must be remembered that we may get two non-conformable points in the vicinity of a change. Sometimes the somewhat less exact method of taking the mean of every two consecutive differential points has been adopted.

Considerable difficulty has been experienced in finding any satisfactory method of depicting the curves in print. The size of the original working drawings is such that their reproduction here would be impossible, without considerable, and often injurious, reduction; this, and the inevitable inaccuracy of printed plates, made it evident that any one wishing to examine the results in detail would plot the experiments out for himself and draw his own curves, while, to the more casual reader, small illustrations in the form of woodcuts would be more instructive and convenient than plates. Such woodcuts, therefore, have been used almost exclusively; but their size generally precludes the insertion of the numerous experimental points, and also necessitates the use of relative scales for the abscissæ and ordinates different from those which are suitable to the experimental error: they may sometimes, therefore, give an exaggerated impression of the magnitude of the changes, sometimes the reverse: I have supplemented them, however, with a statement of the scales which I have found most suitable in the various cases—Table XXIV at the end of the paper.

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* Though differentiation will alone tell us the precise nature of any curve, I would, with the experience I have gained, generally trust as much to the drawing of the original curve as to differentiation, for showing whether that curve is continuous or not, and where the changes occur in it; but such a method would carry conviction to no one who had not made curves their special study to the same extent as I have done.

I must warn my readers that many of the individual changes in curvature which I mention, are admittedly of a very doubtful nature, especially when considered by themselves. Their existence can only be established by the concordant indications of independent properties, and, even with such accumulation of evidence, some of them must still remain doubtful. This is inevitable, if these changes are really due to the existence of hydrates of different degrees of complexity and stability. A study of any one portion of this paper without reading Part VII, where the results from various sources are collected and discussed, would probably lead to a very incorrect estimate of the value to be attached to the work in general, and to the conclusions which I draw from it.

Before proceeding to the details of the work, I must express my best thanks to Mr. H. Crompton for the help which he has so ungrudgingly given me in it. Not only has he made many important suggestions which will be specially noticed in their proper places, but, throughout the course of the work, he has aided me with his superior mathematical knowledge, and followed every step in the work with an interest which has almost made it his own.

PART II.—DENSITIES.

Method employed.

The piknometer is nearly always an inaccurate instrument, owing to the imperfect fitting of the stopper into the neck of the bottle, but the very nature of this inaccuracy implies that it may by chance be non-existent in some cases. Such an instrument was used in the following work. The concordance of the results obtained with it were found to be as nearly as possible the same as in the case of

Sprengel tubes,* and the errors noticed were less than might be attributed to the balance and thermometer errors, these latter being 0·0001 gram and 0·004° respectively. Consecutive determinations of the water contents (25 c.c.) of the bottle at the same temperature only once showed a difference of as much as 0·00015 gram, and a more trying test of its trustworthiness was found in the comparison of my results with water at every 2° between 6° and 38° (to be given in a subsequent communication) with the smoothed curves representing those of Kopp or Pierre; the average difference was in each case 0·000012 of the volume, or 0·0003 gram, and, not only does this error include that due to differences in the determination of the actual temperature, but it was evident that the greater part of it was due to some constantly increasing source of error, which would either be absent in a series of determinations done at the same temperature, or, if present, would have no appreciable effect on the differences between the consecutive experiments, the only important consideration in the present case.

To obtain this accuracy it is necessary to place a small glass plate over the open capillary in the stopper while the bottle is in the bath, and being weighed,† otherwise an appreciable loss occurs through evaporation, even when the liquid is below the bottom of the stopper. The increased accuracy obtained in this way may be judged by the following values, obtained when the bottle was filled with water:—

A. Without the plate—

Extreme diff. of 0·0006 gram in 4 determinations at 8°
" 0·0005 " 5 " 18

B. With the plate—

Extreme diff. of 0·0001 gram in 3 determinations at 8°
" 0 " 2 " 18
" 0 " 3 " 28
" 0·00015 " 5 " 38

The calorimeter, with its stirrer worked by an electromotor, was used as the bath, a very small flame being placed under it when temperatures above 18° were required; at, and below 18°, the temperature of the laboratory was reduced to that of the determinations. The thermometer was tapped continuously as in calorimetric work.

Experimental Error.

The water contents of the bottle were generally determined at the beginning and end (sometimes more frequently) of a series of determinations, and any slight variation noticed was assumed to have taken place regularly. The tare of the bottle was taken before and after each day's work, and rarely showed any alteration. Thus each determination is practically dependent on one weighing only, and the error of the first differentiatial deduced from two determinations is generally of the same magnitude as that of a single determination, since there is generally a difference of 2 per cent. between the strength of every two consecutive solutions, and the actual differences and their errors will be divided by 2. An error of one estimation figure in the reading of the thermometer (0·1 mm. or 0·004°) will, in an extreme case (with acids of high strength and high coefficient of expansion), cause an error of 0·0001 gram; the balance error may be placed at a like amount; so that 0·0002 gram, or 0·000008 of the density, may be taken as a safe limit of error in the majority of cases, both for the determinations themselves and for the differential points deduced from them. With solutions above 78 and below 10 per cent., the differences were less than 2 per cent., and the error in the differentials here will be proportionately larger.

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* Dr. Perkin's and Dr. Nicol's results were taken for this comparison.

† A cap cannot be used while the bottle is in the bath, as it increases the evaporation, or rather, distillation, from the capillary.

The glass plate on the stopper of the bottle was not adopted till after the series at 18° had been finished, so that the error with these results will be somewhat greater,* and another source of inaccuracy in this case was, that the contents of the bottle were determined once for all, it not having been ascertained at that time that a change of a few degrees will effect an alteration in the capacity of a well-seasoned glass bottle (see *Phil. Mag.*, March, 1890). It would, however, be excessive, I think, to place the error of the determinations at 18° at twice the value of those at the other temperatures.

Temperature of the Determinations.

The exact temperatures at which the densities were determined were 7·978°, 17·925°, 28·064°, and 38·203° ± 0·002. All these were ascertained by a direct comparison of the experimental thermometers with a "natural standard," the zero point of which had been recently determined; the "constant difference" of this instrument was taken to be the distance between the boiling point and freezing point, taken immediately *after* boiling, and Poggendorff's correction was applied to the readings.

To reduce my determinations of the water contents of the bottle to true densities, Kopp's determinations of the latter were taken; these are 0·999890, 0·998712, 0·996353, and 0·993070 at the four temperatures respectively. By mistake, the density at 17·925° was taken as 0·998695 in the calculations, but this error will scarcely affect the densities themselves, and will not affect the differentials at all.*

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* It would not, on an average, be nearly so much greater as the above quoted determinations with the more volatile water would imply.

Preparation of the Solutions.

I am indebted to the kindness of Dr. Messel for a liberal supply of the pure acid, prepared by repeated crystallisation. Mr. Crompton was good enough to estimate its strength volumetrically, starting with pure silver. His results, deduced from the examination of two weaker solutions prepared from the strong acid, were—

$$\text{A.}\left\{\begin{matrix}99{\cdot}953\\ 99{\cdot}816\\ 99{\cdot}704\\ 99{\cdot}857\end{matrix}\right\}= 99{\cdot}8325 \text{ per cent. } H_2SO_4.$$

$$\text{B.}\left\{\begin{matrix}99{\cdot}753\\ 99{\cdot}962\\ 99{\cdot}854\\ 99{\cdot}897\end{matrix}\right\}= 99{\cdot}8665 \text{ per cent. } H_2SO_4.$$

$$\text{Mean} = 99{\cdot}8495 \text{ per cent. } H_2SO_4.$$

The value was taken as 99·85 per cent.

The second half of this lot of acid (which had been supplied in two bottles) appeared, from a comparison of about 20 density determinations at 18°, to be 0·007 per cent. stronger than the first half (the one analysed), and, as this small difference could not have been distinguished with certainty by further analysis, it was determined by these density results themselves.

Subsequent work has led me to conclude that the strength of the acid used in the present work is somewhat greater than I have taken it to be. In plotting out the freezing points of a series of acids containing somewhat more water and more anhydride than H_2SO_4 itself, we get a figure consisting of two nearly straight lines rising up so as to meet at a very sharply marked angle, and the point at which they meet must correspond, for reasons which I need not enter into at present, to the definite compound H_2SO_4 itself; the point of intersection of these lines may be ascertained to within ± 0·01 per cent. or less. In this way I have determined, by means more reliable than any analysis, the strength of a large quantity of acid used in subsequent work, and I have compared this acid with that used in the present work, the contents of the second bottle above mentioned being taken for this purpose. The comparison, made by taking the densities of 52 and 66 per cent. acids at 28°, gave

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* It has been corrected in Table VII.

99·92700 and 99·92914, mean = 99·92812 per cent., as its strength, instead of 99·857, given by the analyses. This result was further confirmed by determining its freezing point, which gave 99·932 ± 0·01 per cent. as the strength.*

As all the present results had been calculated out long before this later work had afforded this more certain means of ascertaining the strength of the acid, and, as the error would not appreciably affect these results when differentiated, I did not think it worth while to alter them, except in a few cases, where the introduction of the correction will be specially mentioned. In all the other cases the percentages quoted are 712/1000000 too low.

The accurate dilution of very strong sulphuric acid is not an easy matter. Three main series of solutions were prepared as follows:—

Series A. By exposure to moist air for a month, with subsequent addition of water. Used for about every other determination of the heat of dissolution.

Series B. By addition of ice. Used in the majority of the density determinations at 18°.

Series C. By the very cautious addition of water. Used in the other density and heat of dissolution determinations.

The solutions were made up in quantities of 100 to 200 grams, using a balance reading to 0·0001 gram, so that their relative composition is accurate to about one unit in the fourth decimal place of the percentage, provided no loss of anhydride occurred in making them.

In the case of all three sets, the solutions from 58 to 16 per cent. were made from a 58 per cent. solution; those from 16 to 4 per cent.; from a 16 per cent.; those from 4 to 1, from a 4 per cent.; and the weaker ones from a 1 per cent. solution. To ensure uniformity in the whole series, including the last determination—that is, the one with water itself—this water was boiled in platinum at the same time as that used for diluting the acid, and kept for the same time in bottles of the same glass as those containing the acid. Although this water evidently contained air, not the slightest difference (that is, less than 0·000004) could be detected between its density and that of freshly-boiled water.

Results obtained.

The densities (not specific gravities) at 18° are given in Table I: the full series, with differences not less than 1 per cent., are first entered, and then the more numerous ones with strong and weak solutions: the differentiation of alternate experiments (A and B) are given in the last four columns.* Table II contains the results at 8°, 28°, and 38°, the differentiation of alternate experiments being here given (in the few instances where it is adopted) separately.

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* Some acid prepared by W. Kohlrausch (*Ann. Phys. Chim.*, 17, 69) by crystallisation gave almost exactly the same results as my stock acid, 1·8342 against my 1·834185 at 18°. Perkin found the density of some supplied to him by Messel to be 1·83748 at 15°, my acid being 1·83726 at this temperature (Trans., 1886, 783).

Fig. 1.—Densities of Solutions of Sulphuric Acid.

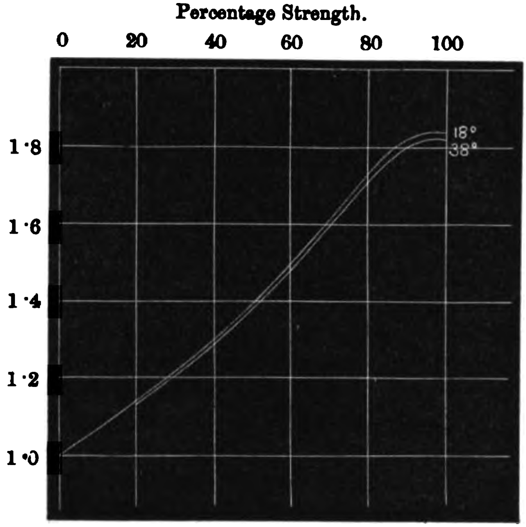

Fig. 1 is a sketch of the densities at 18° and 38° plotted against percentage composition. The general change in curvature at about 80 per cent., and the existence of a maximum at 97·5 per cent. are noticeable, being ignored by most text-books.

Fig. 2, A (p. 80), gives a small size illustration of the first differential obtained directly from the results at 8°. Plates 1 and 2 (p. 184) show this, as well as the results at the other temperatures, on a scale more appropriate to the experimental error and inclination of the various parts of the figures.

At 28° and 38° it was found impossible to extend the determinations below a 20 per cent. acid, owing to the liberation of air-bubbles, and the densities at these temperatures, even from 30 per cent. downwards, may be affected (though apparently with regularity) from this cause.

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* Where two solutions of nearly the same strength have been examined, the results with each have been differentiated separately with those of the next stronger and next weaker solutions; we thus get two pairs of partially independent differential points at nearly the same percentages. This is a more accurate method than taking the mean of the two experiments themselves. Those solutions marked by an asterisk belonged to different sets of preparations from the others.

In each of the plates (1, 2, and 3) the experimental error of 0·0002 gram, or 0·000008 of the density, would alter the position of the points by about one hundredth of a big division of the paper. Greater errors evidently exist in some cases, and are probably due to errors in the composition of the solutions. By the omission of the doubtful determinations we get the points, marked by crosses (the "alternate determinations" of the table), each of which, it must be remembered, is a substitute for the two points on either side of it, and considerable assistance in determining where such mean points should be taken, is afforded by the fact, that the solutions used at 18° were, in nearly all cases,* different from those used at the other temperatures.

Starting at the 100 per cent. end, we have, in each case, a rapid rise, represented by a line of a strongly-curved nature, as far as about 94 per cent.; this is then followed by a long, and comparatively flat stretch as far as 84 per cent., it being so flat in the case of the results at 18°, that it is within experimental error a straight line. Then follows a more or less sharp curve, which gives place to a gentler curve: the differential reaches a maximum point at about 73 per cent., and then proceeds to fall, but not regularly, for it forms a most unmistakably wavy line, exhibiting two troughs at about 42 and 3 per cent. respectively, after which it rises again in a very abrupt manner.

Now, even the most general characteristics of this first differential are absolutely conclusive as to its not being rectilineal, and not being a single or simple curve, and, consequently, that the densities themselves cannot be represented by any single curve. No amount of smoothing could mask the wavy character of three quarters of the figure, or could reduce it to uniformity with the flat portion from 84 to 94 per cent., and with the abrupt curvature exhibited at both extremities.

Although the figure may be continuous, it can only be drawn in separate sections or curves; but to determine the exact nature, or even number, of these constituent curves, is a difficult problem. A good deal, but, as will be shown below, not so much as might be expected, depends on the amount of smoothing allowed. In the present drawing this smoothing is sufficient to render the whole figure continuous, and to allow considerable latitude beyond the known experimental error: no greater amount of smoothing is legitimate in the first instance, and could be justified, only in the event of the present drawing leading to contradictory, or to no conclusions.

The constituent curves of the figures have been extended beyond the points up to which they are applicable, simply in order to show more clearly which portions have had to be drawn separately. These constituent curves, in some instances, cut each other on being produced, but, in the majority of cases, they appear to meet tangentially. Curve VIII, Plate 2, between 50 and 60 per cent., is of a very doubtful character, chiefly owing to the error in the 60 per cent. solution: it does not, however, appear possible to draw curves VII and IX so as to meet without increasing the error of the points very considerably; they apparently cease to be applicable at about 50 and 60 per cent. respectively, and hence curve VIII has been drawn to represent the points between these two percentages. With Fig. D especially, this curve is very doubtful, since there may be another error at 58 per cent.; there is also some doubt as to the drawing of curve VII.

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* Except at 5, 7, 9, and the odd percentages from 79 upwards.

The two series of determinations at 18°, with totally different sets of solutions (A and B, Table I), when plotted out separately, show a concordance which affords strong additional proof of the correctness of the results.

The more numerous results with weak solutions (F and G, Pl. 2) show some remarkably abrupt changes, the exact position and nature of which must, however, be doubtful, owing to the magnitude of the error consequent on the proximity of the determinations.

The results with very strong solutions at 18° and 8° (F and G, Pl. 1) show the existence of a change of curvature at about 97·5, which did not appear in the 1 per cent. series owing to lack of sufficient points.* The alternate determinations only have been differentiated in this case; but, even then, the error is three times as great as with the 1 per cent. series.

The direct first differentiation having failed to reduce the densities to a rectilineal figure, the effect of a second differentiation was examined, the operation being performed on the first differential curves. Table III contains the numerical results.† A general review of them is given in Fig. 4, B (p. 87), while A, B, and E, Pl. 3, represent them in greater detail, and on more appropriate scales. The results at the other temperatures closely resemble those at 18°, which alone are represented in the plate. The constituent lines are prolonged in the drawings to render the points of junction clearer.

The second differential diagram is certainly composed of lines which are straight within experimental error,[*] though it is not possible to affirm that they are absolutely straight, or that they may not be united with each other by short curved reaches. Each portion of the first differential figure which had to be drawn separately yields an independent straight line for the second differential, the only exceptions being (1), in the case of curves VII and XII at 8° (not shown here), which, on the second differentiation, yielded (though doubtfully) two straight lines meeting at 40 and 88 per cent. respectively; (2), in the case of both extremities of the figures, where the second differentials are undoubtedly curved: but by being so they really afford strong confirmation of their rectilineal character; for the ends of the 1 per cent. first differential series are, as a matter of fact, made up of one or two points taken from different contiguous curves, and, when we take for the second differentiation points sufficiently close to each other, we find that these end curves split up into straight lines. The results are shown by Fig. E, Pl. 3 (p. 184), and by the discontinuous lines in Fig. F, Pl. 3; the irregularity in the line 1 of the latter is probably due to error.

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* If, however, a sufficient number of readings be taken from the continuous and apparently regular first differential curve for the 1 per cent. series between 94 and 100 per cent., a second differential is obtained which consists of two straight lines meeting at about 97·5 per cent., showing a change here, in a similar, though not so precise a manner, as when we start with a curve containing all the experimental points.

† In the values in this, and some of the other tables, the decimal point has been moved six places to the right ,to economise space.

The following table gives the percentages at which the changes of curvature occur. The determination of their exact position is a matter of considerable difficulty; if the curves constituting the first differential are tangential to each other, the second differential lines will meet *at* the point of change, but if they are not tangential, but

TABLE A.—*Position of the Changes in the Density Curves for Sulphuric Acid.*

At 38°.	28°.	18°.	8°.	Mean.
		97·2 (97·2)	97·7 (96·8)	97·5 (97)
93·5 (94·5)	94·0 (94)	93·6 (94)	94·0 (95)	*93·8 (94·1)
— (89)	— (88·5)	— (89)	88·0 (?) (88·7)	88·0 (?) (88·8)
84·4 (84)	84·5 (85)	84·5 (84·3)	84·5 (83·5)	*84·4 (84·2)
78·2 (78)	77·5 (79·8)	78·0 (77·5)	79·0 (79)	78·2 (78·6)
72·8 (71)	73·3 (69·5)	72·8 (71)	73·3 (71)	73·05 (70·6)
59 (58·5)	57 (62?)	58 (59)	58 (?) (60)	*58·0 (59·9)
49 (none)	50 (49·5)	51 (51)	51 (51)	50·3 (50·5)
— (42)	—	— (38·5)	40 (?)	40·0 (?) (40·3)
32 (31)	29 (28·5)	29·5 (29)	30 (34?)	*30·1 (30·6)
		18·5 (19)	18·5 (19)	18·5 (19)
		8·8 (9·5)	10·5 (9·5)	*9·7 (9·5)
		4·0	3·75	*3·9
		1·05	1·05	1·05
		0·35	0·25	*0·30

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[*] The error may be best estimated from the portion marked XII, Pl. 3; the points in it should lie on an horizontal line, since they are derived from the first differential, which was here drawn as a straight line.

cut on prolongation, the second differential lines will not meet at these points, and may not meet at all. The majority of the curves appear to be tangential to each other, but this is not always so, and, consequently, the meeting points of the second differential lines may give erroneous results. The position of the changes has, therefore, been determined from an inspection of the first differential diagram. Those which I consider to be best established are marked by an asterisk.

The values given in brackets are of some interest. The differentiation of all the densities for different temperatures was worked out at first entirely independently of each other. Each set of results standing by itself, there were no grounds for regarding any particular points as anomalous, and, consequently, the drawings were made with much less smoothing than at present. Yet the position of the changes deduced from them agrees in almost every particular with those deduced from the later drawings. The former values are those given in brackets. The indication of changes at 88 and 40 per cent. (where, however, other results prove such changes), and the low position of the change at 73 per cent.,* are the chief points where any material differences exist.

An investigation of a portion of the results at 18°, to test the possibility of drawing the first differential in sections other than those here given, was made by drawing the portion between 35 and 81 per cent. in sections of which the middle points coincided with the points of change given in the table. Omitting three determinations, which are evidently erroneous, it was found that the average error of the differential points according to this second drawing was 0·000008, as against 0·000004 according to my original drawing, and that the arrangement of + and − errors told against its correctness even more than the increased magnitude of the error. Its adoption would suppose the existence in 23 determinations of 16 errors greater than the liberal estimate of 0·000008 given on page 75 as a maximum. A similar comparison was also made by deducing equations from the points themselves instead of taking drawn curves, but the increase of error was even greater according to this method. The portion of the figure examined, it must also be noticed, is one in which the changes are admittedly but feebly marked, if not as regards their existence, at any rate as regards their exact position.

The conclusions which I draw from these density results, taken by themselves, may be briefly stated as follows:—The direct first differential coefficient forms a continuous but complicated figure, which can only be drawn in separate sections: it does *not* follow from this that each of these sections represents a definite and distinct curve; but, in the fact that each of these sections—differing considerably from each other as to their curvature—on further differentiation gives a straight line, and, in the fact that the results at different temperatures all indicate changes at the same points, we have strong presumptive evidence that such is the case, but this presumption can only be converted into proof by finding that other independent properties, and curves of a different nature, exhibit similar changes at these same points.

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* The determination of the position of the change here is difficult, owing to the general change in the direction of the differential in its neighbourhood. This portion has been plotted out on many different scales, and the mean result taken.

My conclusions as to the nature of the first differential of the densities are in direct opposition to Mendeléeff's. He first represented it as a continuous curve (*Ber.*, 1886, 379), but subsequently (*Zeit. physikal. Chem.*, 1, 275) represented it as rectilineal, Fig. 2, D (p. 81), being a carefully enlarged reproduction of his later drawing. Above it, Fig. 2, C, I have plotted the values which he quotes, and of which Fig. D was given as a representation. That these points show the existence of more or less abrupt changes of curvature in certain regions is evident, but I am unable to see how they can be made to harmonise with Fig. D.*

Mendeléeff's values (deduced from the observations of other physicists) are given in Table IV, together with a slight modification of them, introduced so as to make them more strictly comparable with my own (the want of analogy being merely due to the fact that the actual differences are greater than with mine), and these are plotted in Fig. E, Plates 1 and 2, where they show such a very good general concordance with my own results† that they may be taken together with the latter as affording a further illustration of the effect of temperature on the figure.

Contraction on Mixing Sulphuric Acid and Water.

At the suggestion of Professor Foster, I calculated, from the densities at 18°, the contraction which occurs on mixing the acid and water in various proportions (Table V).

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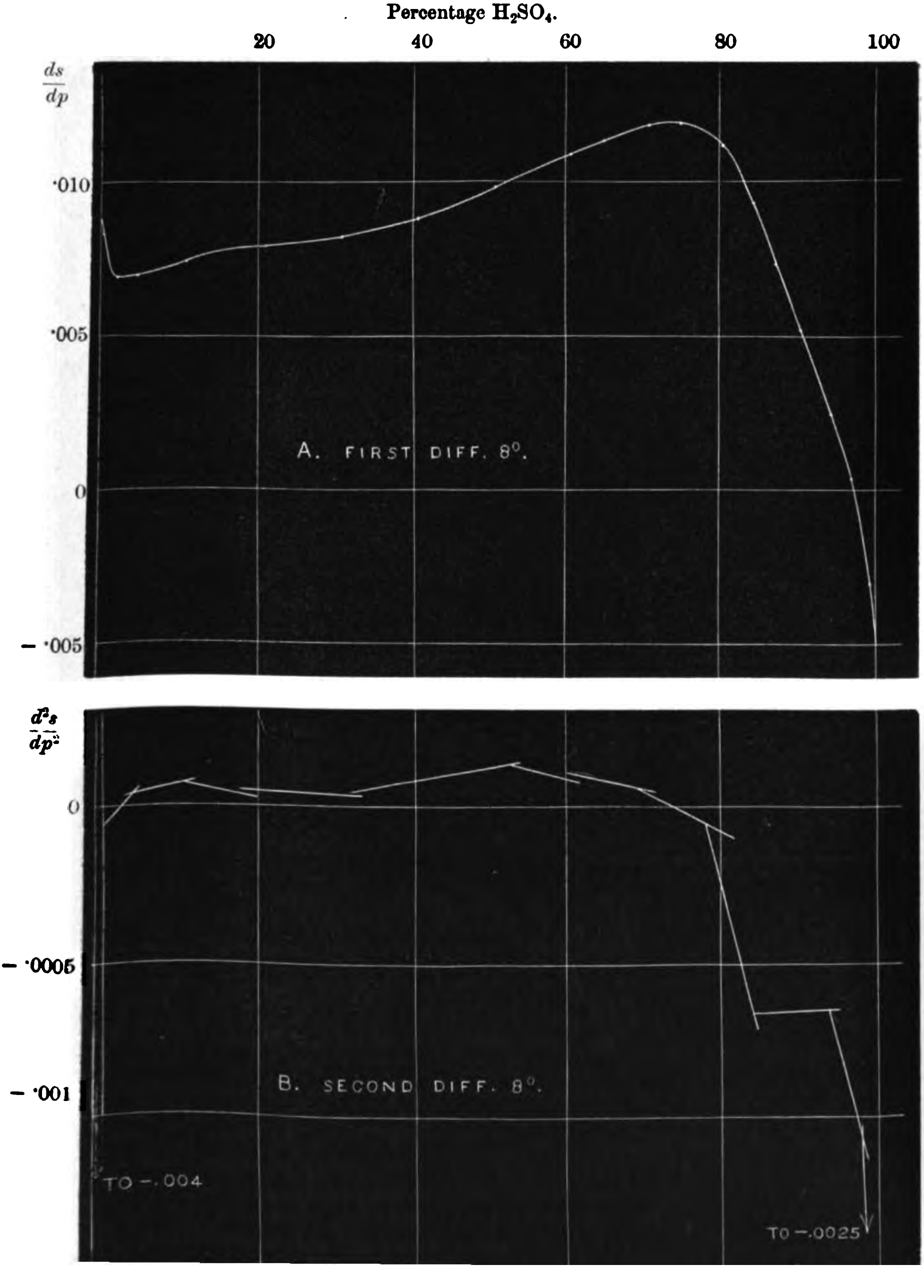
* Mendeléeff inferred from his mathematical theory of the effect of hydrates in solution that the first differential would be rectilineal, and *subsequently* quoted experimental results in support of this conclusion (see Trans., 1887, 779). A study of his drawing of his own results with alcohol leads to the same conclusions as in the case of his sulphuric acid diagram.

A reproduction of Mendeléeff's first curvilinear drawing of the sulphuric acid differential will be found in the *Phil. Mag.*, 28, 33; it forms a striking contrast with his second drawing, and also with the experimental points.

† The point at 57·5 per cent. alone seems to be somewhat erroneous.

FIG. 2.—Differentiation of the Densities of Sulphuric Acid Solutions.



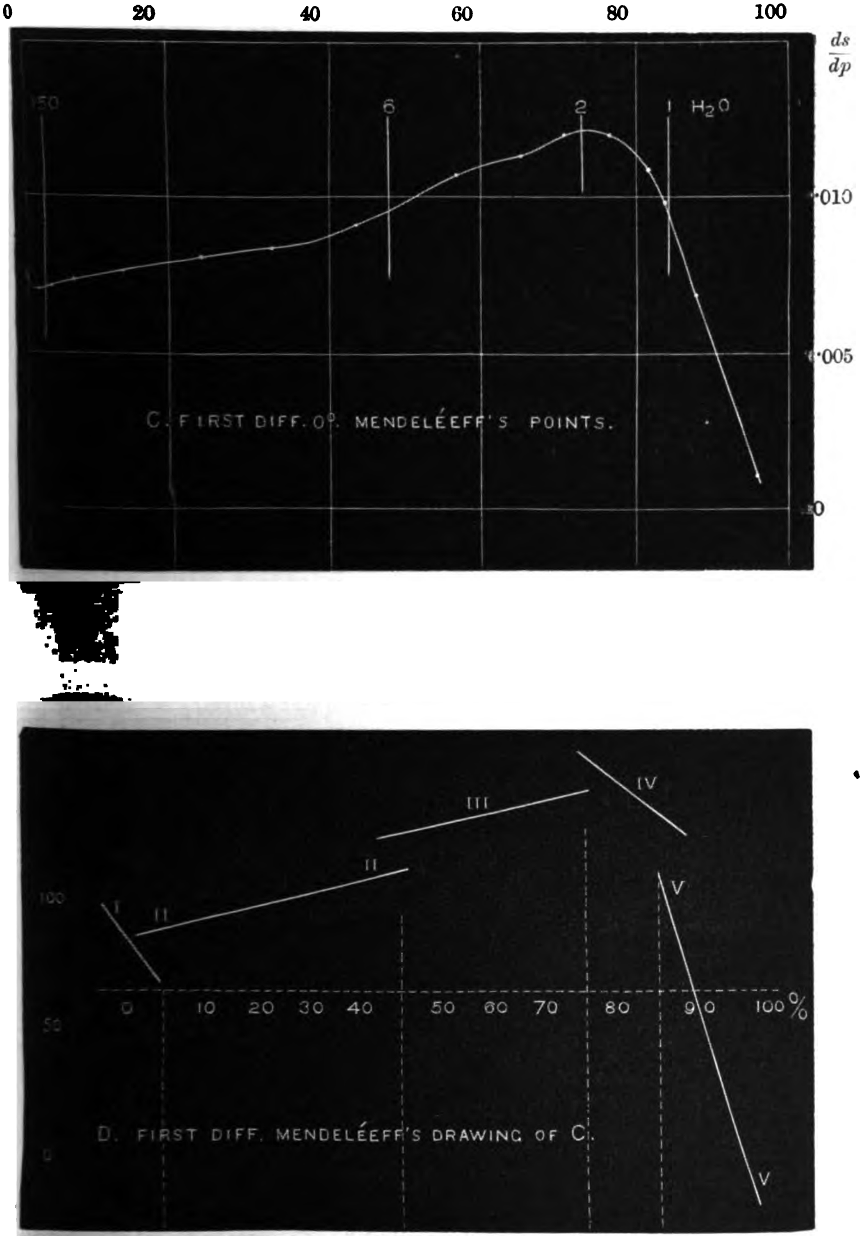
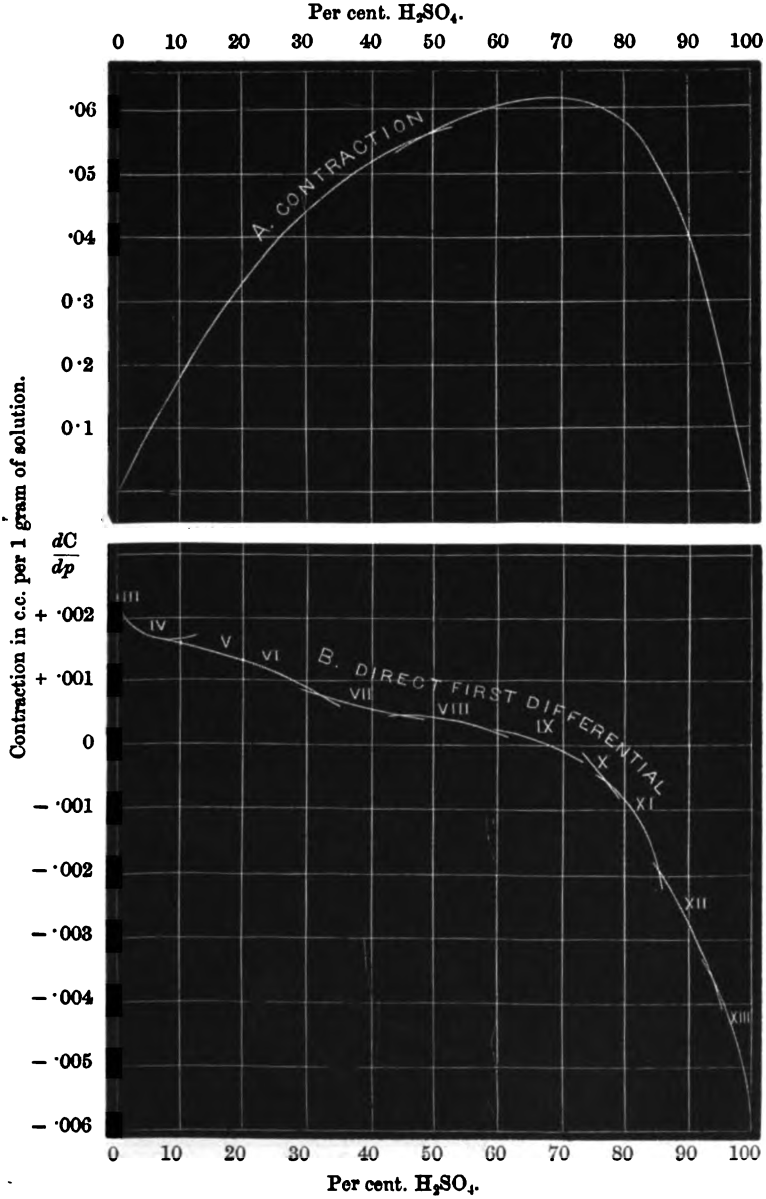


Fig. 2.—Differentiation of the Densities of Sulphuric Acid Solutions.

The figure which these results form is, as in the case of the densities, too large for convenient manipulation. Fig. 3, A represents it

FIG. 3.—Contraction on Formation of Sulphuric Acid Solutions.



on a small scale. It is a continuous, though irregular, curve, attaining a maximum at 68 per cent., and exhibiting a few more or less sudden changes of curvature, of which one at about 50, and one somewhere below 1 per cent., are the most marked.

The first differential obtained directly is illustrated by Fig. 3, B, and, like that of the densities, can only be drawn in separate sections. A second differentiation was performed on this figure (Table VI), and the results are depicted side by side with the second differential of the densities in Plate 3. The general similarity,* though not identity, of these two figures is very striking, and, having been obtained from two figures (the first differentials) which differ entirely in their general character, afford very strong evidence that the rectilineal nature of the figure, and the position of the changes which they both indicate, are true characteristics of the properties in question, and not the chance outcome of the taste of the draughtsman.

The extension of the curvature of the end portion of the contractions from 0 per cent. to solutions of greater strength than in the case of the densities, is but the result of fewer points having been taken in the former: the curve here, and that at the 100 per cent. end, splits up into separate lines when all the determinations are plotted out, but the results are not illustrated here. The drawing of the portion X is very doubtful. The similarity of the two figures would be somewhat increased by taking the contractions on the formation of 1 c.c. (Columns 5 and 10, Table VI), instead of on 1 gram: the results would at 0 per cent. occupy the same position as those for 1 c.c., whilst at the 100 per cent. end they would occupy the position indicated by Fig. F in Plate 3.

The position of the changes of curvature indicated by the contractions and densities at 18° are as follows:—

Densities.	Contractions.	Densities.	Contractions.
97·2	97·6	51·0	47·0
93·6	93·6	29·5	31·0
84·5	85·5	18·5	19·0
78·0	78·8	4·0	3·9
72·8	74·0	1·05	0·95
58·0	60·0		

The concordance between the two sets of results is very good, and would, no doubt, have been better, had the contractions been plotted out on as many different scales, and been worked up with the same care as the densities.

Two points of importance may be noticed. (1.) The constituent curves of the first differential of the contractions are different in nature from the corresponding ones of the densities, since they do not meet tangentially. (2.) The maximum of contraction does not occur, as is generally supposed, at the dihydrate, 73 per cent., but at about 68 per cent., and does not coincide with the position of any sudden change of curvature.[*] It will also be noticed that the changes in the first differentials are more clearly marked with the contractions than with the densities, but I doubt whether this advantage would not be more than compensated by the increased calculations, and consequent chances of mistakes, which the former necessitate.

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* In working out these results I was (and still am) in ignorance that such a similarity should exist.

Construction of a Table of Densities.

The determinations which had been made of the densities of sulphuric acid afforded the means of constructing a fuller and more accurate table than any which existed. The special advantages which they offered for this purpose were (1) that the composition of the acid had been determined by a more certain method than mere analysis; (2) that the very numerous solutions taken were of a composition very near to round percentage values; (3) that such small corrections as were necessary to reduce them to such, could be applied with the greatest accuracy, now that the rate of change with the composition (that is, the first differential) was accurately known.

The various steps in the construction of this table (Table VII) were as follows:—

(1.) The densities at 17·925° were corrected so as to refer to water as 0·998712 (p. 71).

(2.) The percentage strength of the solutions was altered in accordance with the determinations based on the freezing points by being raised 712 millionths (p. 73).

(3.) The few obvious errors which the first differential diagram had revealed were corrected.

(4.) The values for round percentages at 7·978°, 17·925°, 28·064°, and 38·203° were deduced from the experimental values by the help of the first differential figures (Plates 1 and 2).

(5.) To detect and correct any arithmetical errors which had been made in doing so, each of the four sets of results was differentiated, and the resulting figures compared with those in Plates 1 and 2.

(6.) The results at the two higher temperatures did not include determinations above 9·6 per cent. at less than 1 per cent. intervals, nor did they extend down to percentages below 20. The former were supplied by plotting out the densities from 96 to 100 per cent., and taking readings at the required points from the curves thus obtained. The densities below 20 per cent. were supplied by a more doubtful process :—The differences between the densities at 17·925° and 7·978° (an interval of 9·947°) were plotted out, and two curves drawn by their means; a smoothed curve (1) utilising only the differences between 29 and 20 per cent., together with that of 0 per cent.; an irregular curve (2) following the irregularity of the points from 29 per cent. downwards; the differences (*d*) between these two curves (0·00009 of the density at most) were taken at intervals throughout. Then the differences between the densities at 38·203° and 17·925° (an interval of 20·278°) were plotted out, these giving a curve 1′ similar to 1: by assuming the differences between curves 1 and 2 to be proportional to the intervals of temperature, we get the curve 2′ for these last determinations by multiplying the differences, *d*, by $\frac{20{\cdot}278}{9{\cdot}947}$ and adding the result on to the readings of curve 1′; in this way the densities at 38·203° were deduced from those at 17·925°, and the densities at 28·064° from those at 7·978°. The values thus obtained cannot be very exact, but, I think, they are probably right to the fourth decimal place.

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[*] The position of this maximum is known to alter with the temperature.

(7.) The densities of each solution at the four temperatures were plotted out on a scale which showed 0·00002 of the densities and 0·02° (the largest scale which could be conveniently adopted); from the smoothed curve representing them, the rate of change was determined, and used for the arithmetical reduction of the densities at 7·978° to 8°, 17·925° to 18°, 28·064° to 28°, and 38·203° to 38°. The values for the other temperatures (every degree from 40° to 0°) were got by taking readings directly from the curves: these would be less accurate than the former.

(8.) As the extrapolation of these curves was extended as much as 8° below the last determination, the values at these extreme temperatures cannot be regarded as more than approximate. Their accuracy was improved by differentiating all the values at 0°, comparing the differential with the figures in Plates 1 and 2, and introducing such corrections as increased the smoothness of the curve.

(9.) Finally, as a check on the readings taken from the curves, the values for each solution at different temperatures were differentiated, and such slight corrections made as would render them more regular.

The accuracy of the values may be thus summed up:—

The percentages represent the truth within about 1/10,000th of their total value: their relative accuracy, however, is probably 100 times greater.

The density values at and near 38°, 28°, 18°, and 8° are more accurate than at other temperatures, but, with certain exceptions, the actual errors are probably nowhere greater than one or two units in the fifth decimal place. The exceptions are, (1) all the solutions at temperatures below about 5° or 6°, (2) solutions of a strength of 30 per cent.* downwards at temperatures above 20°. Here the errors may affect the fourth decimal place.

About one quarter only of the full table is reproduced here; some of the values which are utilised in Part VI are not contained in it, and these are given in Table VII, A.

PART III.—ELECTRIC CONDUCTIVITY.

Crompton's examination of F. and W. Kohlrausch's determinations of the electric conductivity of sulphuric acid solutions (Trans., 1888, 116) led him to conclude that these results, when differentiated a first time, gave a continuous but irregular curve; and, when differentiated a second time, a series of straight lines, meeting at the percentages of 84·4, 73·1, 47·6, 18·5, and 3·5, corresponding to the hydrates with 1, 2, 6, 24, and $150H_2O$, thus confirming the four changes indicated by Mendeléeff's density curve, and showing, in addition, a fresh change at $24H_2O$.

I certainly think that these results, if taken by themselves, would scarcely warrant such conclusions, though perhaps they might in some points add confirmation to Mendeléeff's hydrates, assuming, as Crompton did at the time, that these were already well established. Crompton's results, I found, were also vitiated in parts by various arithmetical mistakes, and I have therefore reproduced his table here (Table VIII) in a corrected form.

Fig. 4, A gives an illustration of my drawing of the direct first differential, drawn, as in the case of the densities, with a bent ruler and having the separate sections prolonged. Fig. 4, B represents the second differential, deduced also directly from the experimental values. This appears to me to be made up of three straight lines and two curves, and the breaks indicated by it correspond in one case only (the monohydrate) with any mentioned by Crompton.

The portion VI does not contain sufficient points to admit of a second differentiation, but the position of the first differential point at 99·7 per cent. indicates the possibility of another change between 99 and 100 per cent.† Besides the breaks shown by the direct

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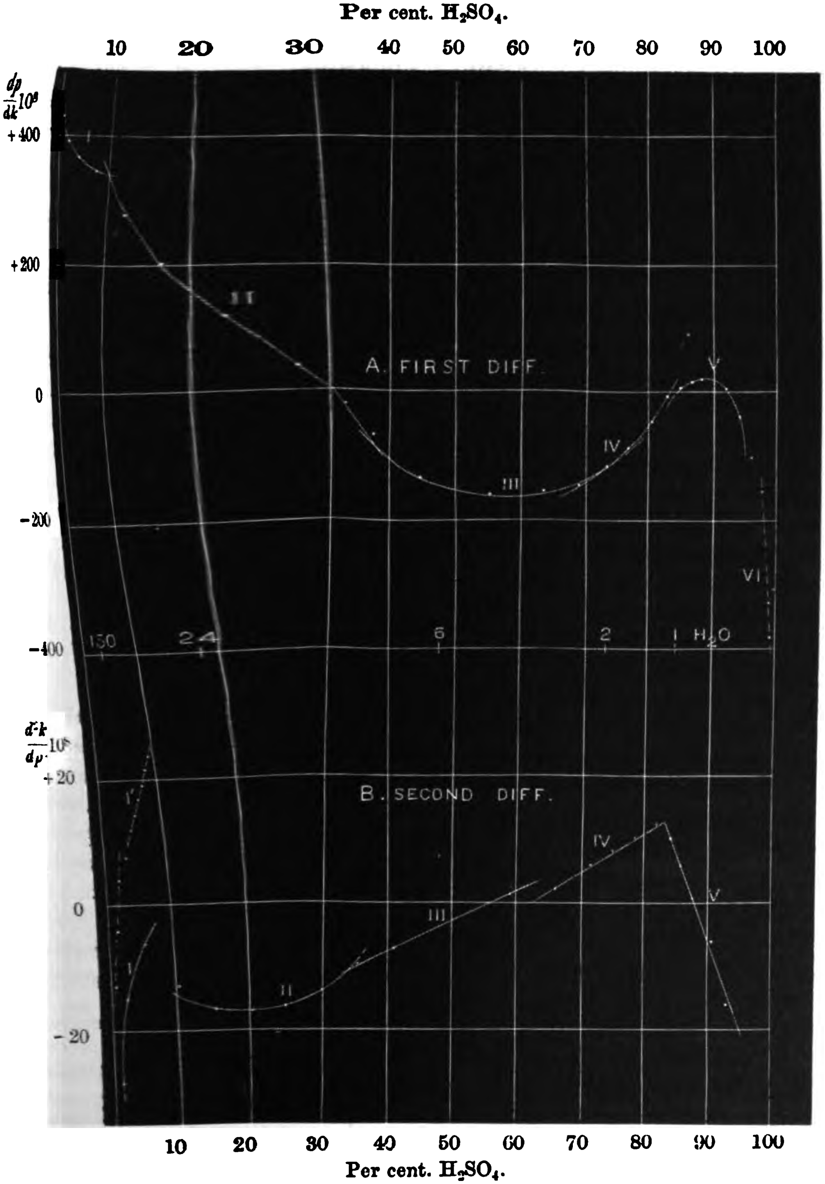
* The actual determinations at 38° and 28° extended down to a 20 per cent. solution, but the possible liberation of air bubbles rendered the results below 30 per cent. somewhat doubtful (see p. 74).

† The values at the higher percentages (marked by an asterisk in the table) were selected by Crompton from W. Kohlrausch's determinations. I have examined the other determinations made by the same physicist, but without gaining any further information from them.

FIG. 4.—Conductivity of Sulphuric Acid Solutions.

Direct First and Second Differentials.



second differential, there appears to be another at about 3·5 per cent., since, by differentiating the first differential *curve* I, I always got a second differential consisting of two straight lines meeting at this point, as shown by I′,* Fig. 4, B.

Considering the paucity of the determinations, and the severe strain put upon them by two direct differentiations, I think that they are fairly conclusive in favour of the second differential being rectilineal, and Crompton has done good service by drawing our attention to this fact.†

The positions of the various changes which I consider to be shown are the following, although the indications can in no case be taken as proof:

99·5, 96·8, 94*, 84*, 63 (or perhaps 73‡), 37·5, 9·5*, and 3·5 per cent.

Those marked by an asterisk are, I think, the best established.

I am glad to be able to state, with Mr. Crompton's authority, that he agrees with me in the criticism which I have here given of these conductivity determinations, and that he considers that the interpretation which he originally put on them must naturally fall through, now that it appears that Mendeléeff was mistaken in his statements as to the densities, for Crompton never regarded the conductivity results as sufficient to stand by themselves, but only as affording additional proof to a theory which had (as he then imagined) been already satisfactorily established by other facts.

PART IV.—HEAT CAPACITY.

The unit heat capacity of a body is measured by the number of units of heat required to raise a unit mass of it 1°; its specific heat is the ratio between its heat capacity and that of some standard substance under the same conditions, the variable standard, water, being generally selected. The two terms are precisely analogous to "density" and "specific gravity;" the former measures a property of the substance, the latter measures the difference between the properties of two substances.

The unit of heat being the amount necessary to raise 1 gram of water from 0° to 1°, it is most important in ordinary calorimetry to know the heat capacity of water at different temperatures. Such determinations as have been made of it show, unfortunately, very large discrepancies, Regnault's results, which are known to have been miscalculated, being generally taken. The value at 18°, deduced from the four most concordant sets of determinations available,* is 1·006; in the present work I took 1·005 by mistake.

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* Placed one division of the paper higher than it should be. The numerical values are given in Table IX.

† The curvature of line II might, perhaps, be reduced to straightness, if we had sufficient points to indicate changes at 9 and 19 per cent., such as my density results show.

‡ According to the first differential, the position of this change might be 63 or 73 per cent., the second differential favours the former view; but a small error in one determination only would alter the case.

The most accurate method of general applicability known for the determination of the heat capacity of weak solutions, consists in dissolving some strong solution of the same substance in water at two different temperatures. The difference in the heat evolved is equal to the difference between the total heat capacities of the reagents (water and strong solution) and that of the resulting weak solution.

$$\mathrm{H} - \mathrm{H}' = (\mathrm{U} - \mathrm{V})(t' - t).$$

To apply this, various quantities of a sulphuric acid solution of 58 per cent. strength† were dissolved in water at 15° and 21° (t and t'): the rise of temperature noticed being r and r' in the two cases, W being the weight of solvent water, w that of the strong solution, w' the weight of the apparatus, and c, c', c'' and c_1 the heat capacity of the water, the strong solution, the resulting weak solution, and the apparatus respectively, we get—

$$[(\mathrm{W} + w)c'' + w'c_1]r' - [(\mathrm{W} + w)c'' + w'c_1]r =$$
$$[(\mathrm{W}c + w'c_1 + wc') - (w'c_1 + (\mathrm{W} + w)c''](t' - t),$$

whence

$$c'' = \frac{(\mathrm{W}c + wc')(t' - t) + w'c_1\,(r' - r)}{(\mathrm{W} + w)\,(r' - r + t' - t)}.$$

A drawback to the general use of this method is, that the heat capacity of the strong solution must first be known; but it need be known approximately only, since an error of 1 per cent. in its value will introduce an error of only 0·0005 in the heat capacity of a 5 per cent. solution, and will affect all the results regularly in inverse proportion to the strength of the solution obtained.

The method assumes that the heat capacity of the liquids concerned is the same at the lower as at the higher temperature. This is not the case; but the difference is very small. Judging by Marignac's results, the difference at temperatures 6° apart would be only about $\frac{1}{5000}$th for most 5 per cent. solutions, and the error thereby introduced would be almost entirely counterbalanced by the heat capacity of the water varying in the same direction as that of the solution.

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* Regnault's recalculated by Bosscha, Baumgartner's, v. Münchhausen's and Henrichsen's. (See Landolt and Börnstein, *Tabellen*, 176.)

† A solution of this strength gives a resulting solution of the maximum strength with the smallest possible rise of temperature.

The determinations were made in the same way as those mentioned in Part V. As it was practically impossible to take exactly the same weight of the strong solution at the two temperatures, the results obtained were plotted out into curves, and the readings of these curves, at points near those at which the actual experiments existed, were taken. Two determinations at least were made near each point.

Two opposite thermometric errors of 0·0005° in the determination of r and r'* would cause an error of 0·00017 in the heat capacity found. With sulphuric acid, the rapid increase in the heat evolved with the amount of strong acid used renders it impossible to plot out the values for this evolution on a sufficiently open scale, and the error may be doubled from this cause alone. This source of error was reduced in the present case by taking the readings for r (and r'), not only from the curves directly representing them, but also from curves in which the values for r/w were plotted out. The error, therefore, in the heat capacities might probably amount to 0·00025,† and, judging by the regularity of the results themselves, it never appears to exceed this.

The determinations were extended to a 12 per cent. solution by a second series of determinations, in which the strong acid was dissolved in a 4·6 per cent. acid, instead of in water. The heat capacity of this solvent acid had been determined by the first series, and the two series were made to overlap.

Results obtained.

The results with the weaker solutions are given in Table X, the experimental values being quoted in the first four columns. The values for r and r' for a round number of grams of solution, w, as determined from the curves directly representing these quantities, are given in the sixth and eighth columns, whilst the mean of these values and those deduced from the r/w and r'/w curves are given in the seventh and ninth columns. With the stronger solutions (Table XI) the values for r and r' were deduced solely from the r/w and r'/w curves.‡

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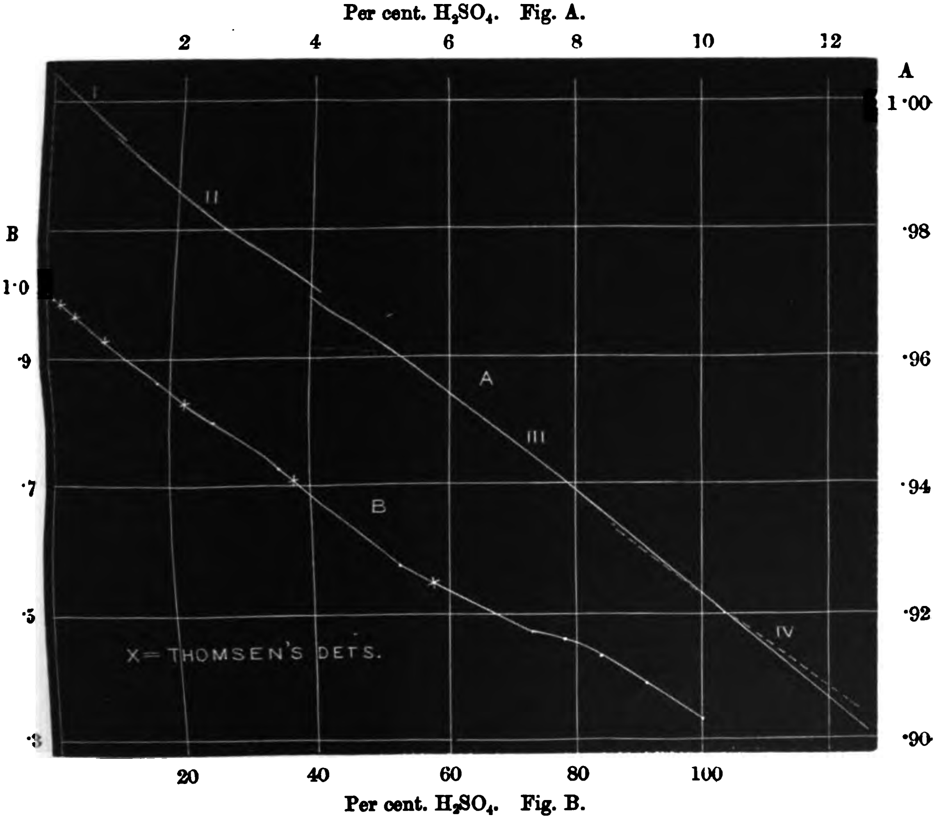
* These, of course, are not dependent on the differences between two experimental values *only*.

† The average difference between Thomsen's duplicate determinations is about 0·003.

‡ Anyone plotting out these values will notice irregularities in the case of r/w

Fig. 5, A illustrates the diagram representing these results. It consists of four distinct curves, of which II and III are the best established; these bend in opposite directions, and do not appear to meet at all. The same want of continuity seems to exist between curves I and II, whilst there are not enough determinations (only two) to settle the nature of curve IV (the dotted line), and whether it touches curve III, or not. There are 4, 9, 11 (three of series 1 and

FIG. 5.—Heat Capacity of Sulphuric Acid Solutions.



eight of series 2), and 2 experimental points on these four constituent curves respectively. The break at 4 per cent. depends on a

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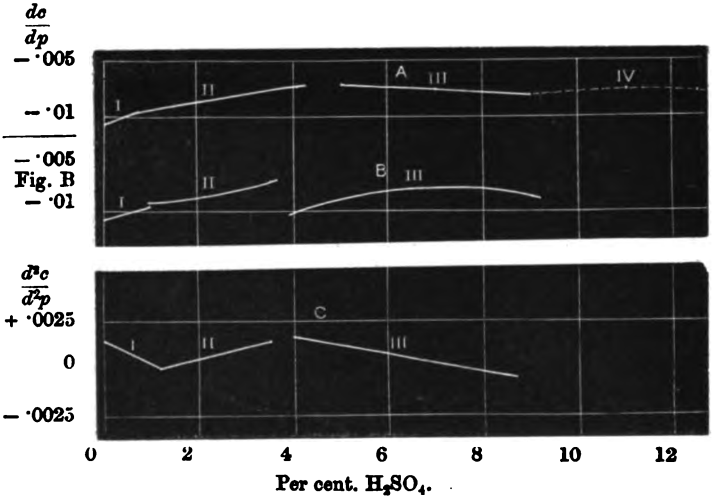
for about 3 grams, and r'/w for about 8·5 grams, which are somewhat too great to be attributed to error. In my drawing I have erred on the safe side, by smoothing out these irregularities. The values in brackets in the table show what differences their not being smoothed out would make.

difference of 0·0013, or five times the experimental error, besides, of course, being established by the general direction of the curves on either side of it: the exact position of the change near 1 per cent. cannot be determined, and, indeed, the recognition of any change at all here is a difficult matter; it is best done by carefully drawing curve II, and producing it to 0 per cent., when it will be found that all the points below 1 per cent. lie above the prolongation.*

The first differential obtained directly (Tables X and XI) is shown in Fig. 6, B: the changes are fairly well marked, but the nature of the constituent curve is somewhat doubtful, owing to the curvature being very small in comparison with the experimental error. A second differentiation (Table XII and Fig. 6, C) reduces these curves to straight lines. Fig. 6, A represents the first differential obtained from the smoothed curve, Fig. 5, A (Table XIII): it differs from the direct first differential in representing the constituent portions I and III as straight lines, instead of curves; this is but a natural result of the process of smoothing, and of the smallness of the differences on which the curvature in this case depends.

FIG. 6.—Heat Capacity of Weak Sulphuric Acid Solutions.

First differential from the curve and from the experiments. Second differential from the latter.



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* In this, and other cases, it is sometimes advantageous to draw some particular curve on a more open scale than could be done accurately by plotting out the experiments themselves. This may be effected by drawing the curve first on a small scale, taking readings from this, plotting these out on a large scale, and drawing a smoothed curve through them.

Whether the heat capacities require one or two differentiations to reduce them to straight lines, must, therefore, be regarded as somewhat uncertain, the evidence being in favour of the latter view.

The positions of the changes are—

9·85, 4·0, and 1·0 per cent.,

of which the first two are very clearly marked.

A point of some interest arises as to these curves. The heat capacity must be a continuous function of the strength of the solution, and hence the drawings here made of the results cannot be correct at the points near 1 and 4 per cent., where the curves are represented as not meeting each other. I think it probable that the main curves, I, II, and III, are connected by short curves of a totally different nature, resulting from, and representing, a state of passage between the different conditions which exist in the main curves. This is supported, perhaps, by the fact that there is one experimental point at 4·1 per cent, exactly between the two curves. No such intermediate condition is noticed in the density or heat results, but in the heat capacity we are studying a property of a nature totally different from that in these other cases; the density is a property under *fixed* conditions, and the heat of dissolution is a measure of a portion of the potential energy in the substance, also under *fixed* conditions, whereas the heat capacity is the work which has to be expended on the substance in order to *alter* its conditions.

The smallness of the difference between the sum of the heat capacities of the strong acid + that of the water (or 4·6 per cent. acid), and that of the resulting weak acid, is noticeable, and might excuse a superficial observer in concluding that no chemical action occurred. In series I we find—

Per cent. H_2SO_4.	c''.*	$c + c'$.†	Diff.
2·67	0·98084	0·98396	−0·00312
5·06	0·96125	0·96510	−0·00385

while in series II the cases of maximum difference are—

Per cent. H_2SO_4.	c''.*	$c + c'$.†	Diff.
8·42	0·93631	0·93611	+0·00020
9·55	0·92668	0·92739	−0·00071

Calculating pure H_2SO_4 (heat capacity 0·3332) and water as the constituents, the differences, though greater, are still small—

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* Heat capacity of resulting solution.

† Heat capacity of components.

Per cent. H_2SO_4.	c''.*	$c + c'$.†	Diff.
3	0·97812	0·98475	−0·00663
6	0·95452	0·96469	−0·01017
9	0·93137	0·94454	−0·01317
12	0·90862	0·93438	−0·02576

Fig. 5, B (p. 91) represents the heat capacities of strong solutions used in the subsequent heat of dissolution determinations, as deduced from Berthelot's table (*Mec. Chim.*, **1**, 496), which collects the values of Thomsen, Marignac, and Pfaundler. Beyond illustrating the general irregularity of this property as a function of percentage composition, and the probability of the more marked changes occurring at about 10, 50, and 73 per cent., they can afford no definite information as to the nature of the figure, through lack of sufficient points.

PART V.—HEAT OF DISSOLUTION.

In 1875 Berthelot (*Ann. Chim. Phys.* [5], **4**, 446) published his determinations of the heat evolved when solutions of different strengths of the commoner acids and alkalis are diluted with an excess of water, and concluded that there were signs of changes near certain points, indicating in an approximate manner the existence of hydrates in solution. His determinations were numerous, but would not seem to be accurate enough for settling the question,‡ even if sufficient data had been quoted to permit of their recalculation into a form suitable for mathematical analysis.

Thomsen afterwards (*Thermochem. Untersuch.*, **3**, 1—114) went afresh over the same ground,§ and also investigated the cases of many salts as well. His conclusions—that the action was regular, and that hydrates higher than those known in the solid form did not exist in solution—were in direct opposition to Berthelot's, and have gained a ready acceptance amongst chemists.‖

Thomsen's conclusions are indeed remarkable. The points determined on each curve rarely exceeded six¶ (sometimes there were only

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[*] Heat capacity of resulting solution.

[†] Heat capacity of components.

[‡] The initial temperatures sometimes varied 4° or 5°, and the heat capacities used were very uncertain.

[§] He had previously (*Ber.*, 1870, 496) investigated sulphuric acid, as also had Hess, Graham, Abria, Favre and Silbermann, and especially Pfaundler (*Ber.*, 1869, 122).

[‖] "The generally adopted 'hydrate theory' of solution can scarcely be expected to survive the dissemination of Thomsen's researches" (P. Muir, *Elements of Thermal Chemistry*, 167).

[¶] And these points were least suited for showing irregularities, since they corresponded to simple molecular proportions (see a remark of Crompton's, *Proc.*, three or four), a number scarcely sufficient for determining even the general character of the reaction, and yet, in many of the cases where they appeared sufficient, they showed that this general character was eminently irregular. In 10 cases out of 53, the value of the reaction changes its sign, in two others the irregularity is palpable, and, even in those actions of greatest apparent regularity, it is found that no simple equation can represent all the results. The equations which express the results with strong solutions generally give values too low when extended to weaker ones* (see *Chem. News*, **54**, 215); nor can they be extended in the opposite direction with any better success. Thus, Thomsen has extended his curve in the case of copper chloride so as to give the heat of dissolution of liquid $CuCl_2,2H_2O$; if he had extended it further still, so as to get the value for $CuCl_2$ itself, he would have recognised the inadmissability of such a process; for the value obtained (9233 cal.) gives, as the heat of formation of liquid dihydrate from its liquid components, 1434 cal., whereas this quantity should be nearly identical with that of its formation in the solid state from the solid components, which direct experiment gives as 3540 cal.† With calcium chloride the case is still more striking. Thomsen's determinations give—

$$CaCl_2,10H_2O + mH_2O = \frac{m}{m + 5{\cdot}08}\ 2{,}508,$$

from which the heat of dissolution of liquid $CaCl_2,6H_2O$ should be 11801 cal., instead of 6640 cal., as my direct determinations prove it to be, and that of liquid $CaCl_2$ should be -3460 cal., a negative quantity, whilst even the *solid* salt gives a positive evolution of as much as 19250 cal.

Thomsen's results with sulphuric acid are of special importance, not only from his having studied this acid more fully than any other substance (12 points were determined!), but that the seeming regularity of these results is for ever being urged against the hydrate theory of solution. The language in which he expresses his con-

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1888, 38, of which Thomsen's values for SO_3 and $SO_3,\frac{1}{2}H_2O$ form excellent illustrations; the former lies within experimental error on the extension of his curve for $H_2SO_4 + nH_2O$, the latter is very far removed from it).

* Thus Thomsen's equation for sulphuric acid is inapplicable beyond $19H_2O$, that for nitric acid beyond $5H_2O$, and that for hydrochloric acid seems to be inapplicable everywhere.

† If the heat of fusion of the hydrated salt is (as Person concluded from the instances which he examined) equal to the sum of those of the anhydrous salt and water present, the identity would be absolute. I think it probable that in many cases this equality does not hold good (indeed there are instances in which it certainly does not), but the discrepancy could hardly make as much difference as in the instances quoted above.

clusions as to the curve representing them is of a most positive and uncompromising character. "One sees," he says (III, 8), "that the fixed points can be united by a regular curve, and that throughout, there are nowhere any signs of an irregularity, such as would indicate the formation of definite hydrates." He then gives the equation for the hyperbola representing this curve, and a table showing the near agreement of the found and calculated values for $H_2SO_4 + xH_2O$, when the values for x are 1, 2, 3, 5, 9, 19, and 1600, and then proceeds, "One sees that the differences are very small, and are positive or negative indiscriminately.* There is, therefore, no doubt but that the heat evolved on diluting liquid sulphuric acid with water is a continuous function of the water used, and excludes absolutely the acceptance of definite hydrates as existing in the solution."

The concordance of the found and calculated values for these seven points is, indeed, remarkably good, but, even if it were absolute, it could scarcely warrant such a conclusion, especially when it is remembered that the portion where this agreement exists is but little more than *one per cent. of his whole curve*,† and that throughout the remaining *ninety-nine hundredths* of it there is no agreement at all, the differences reaching as high a value as 683 cal.

If any conclusions at all can be drawn from Thomsen's work, they must certainly be in favour of the probable irregularity of the actions in question.

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* If the differences between the calculated values and the experimental points are tabulated for *all* of the latter, the indiscriminate arrangement of the + and − errors is by no means apparent. They are—

x =	1,	2,	3,	5,	9,	19,	49,	99,	199,	399,	799,	1599
Diff. =	−3,	+14,	−30,	−27,	+66,	−59,	−544,	−683,	−686,	−467,	−180,	+17

Had Thomsen extended his determinations to more dilute solutions, he would have found still greater differences. My value for $x = \alpha$ (determined by the extension of an experimental curve which reached as far as 0·04 per cent., or 15,000 H_2O) compared with the value calculated by his equation, gives a difference of +3233 cal.

† Measured along the abscissæ, which represent the number of molecules of water added to H_2SO_4: the concordance is exhibited as far as the 19th H_2O: the curve extends to 1599 H_2O. Measured along the curve itself, the relative proportions of the regular and irregular parts would depend on the scale used: with the scale adopted by Thomsen in Fig. AB, Table I, vol. iii, the regular part would measure 1·8 per cent. of the whole figure.

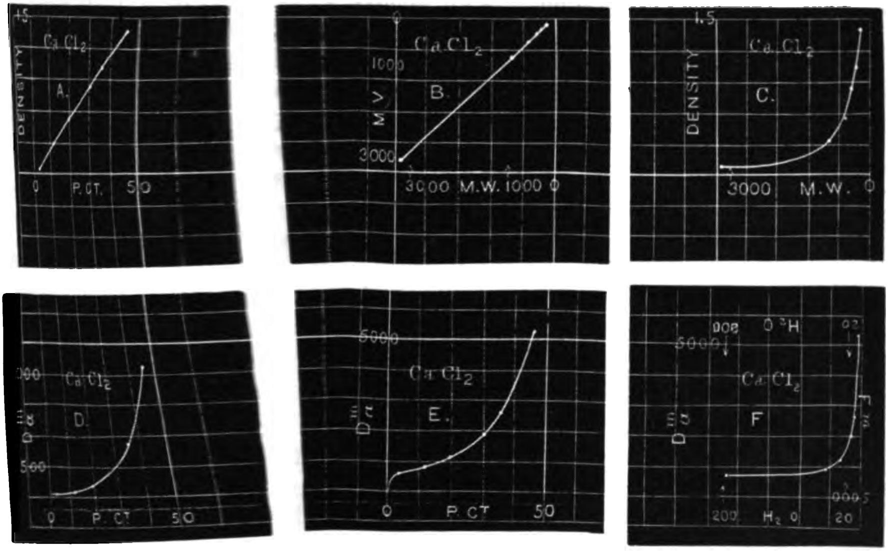
It is but fair to state that Thomsen afterwards (*loc. cit.*, p. 56) suggests that this aberration, which must invalidate his conclusions, may be due to the contraction on mixing, but he offers no evidence in favour of such a view, and no explanation of why the effect of this action should be appreciable only in those cases (weak solutions) where it occurs to the smallest extent.

Graphic Representation of Results.

The question as to the plotting of the results becomes of paramount importance when a mathematical analysis of the curves obtained has to be performed.

The drawings which I give in Fig. 7 refer to calcium chloride, and are better for the purpose of illustration than the more complicated results with sulphuric acid; the heat curves, however, are very similar in the two cases.

FIG. 7.



When the densities are plotted against percentage composition (A), or when the molecular volumes are plotted against molecular composition (B), rectilineal or parabolic figures are obtained in each case, differing only in distribution of the experimental points along them (the same six experiments are plotted in all the figures); but, if we plot the densities against molecular composition (C), or the molecular volumes against percentage composition, we get a complicated hyperbolic figure, most unsuitable for mathematical analysis. Yet such is the method of plotting which has heretofore been adopted in the case of all heat results; the heat of dissolution, or formation, of a *fixed* weight of the dissolved substance (the so-called "molecular" heat of dissolution, but molecular in a sense different from that of molecular volume, since it bears no reference to the molecular composition of the *solution*) being plotted against the molecular composition of the solution. Fig. 7, F (p. 97) represents the heat of dissolution thus plotted; if inverted it will represent the heat of formation (F^m) as plotted by Thomsen.

As any quantity expressing the heat of dissolution in a manner corresponding to "molecular volume" has no meaning (such as molecular weight ÷ heat of dissolution), we must abandon the representation according to molecular composition altogether. I plotted out in the first instance the heat of dissolution of various solutions containing gram-molecular proportions of the salt, against percentage composition (E). On differentiating this, however, no satisfactory results could be obtained, another apparently continuous curve being produced. Mr. Crompton then suggested that, instead of plotting the heat of dissolution of gram-molecular proportions, we ought to take the heat of dissolution of 100 grams of the solution (Fig. D). Satisfactory results were obtained in this way. Similar results would no doubt be arrived at by taking the heat of formation of 100 grams of the solution; such a curve, instead of falling from a maximum down to zero, would start at zero (at the point where no water was present), rise to a maximum, and then fall back again to zero.

Method of Experimenting.

Two classes of determinations were made:—

1. "Mixing" experiments, in which 420 c.c. of the solutions were mixed with successively equal volumes of water. A detailed description of the new mixing calorimeter devised for this purpose, and the method of using it will be found in the *Phil. Mag.*, March, 1890.

2. "Dissolution" experiments, in which 4 to 30 grams of a strong solution were dissolved in 600 c.c. of water (*ibid.*).

Calculation of the Results.

To be comparable, all the results must be calculated out for the same final dilution: this must be not less than that obtained in the determination with the weakest solution used (0·04 per cent.). Theoretically the dilution should be infinite, and the heat evolved for infinite dilution is in this case easily obtained by plotting out the results (for dilution down to 0·04 per cent.) against percentage composition, and extending the curve as far as 0 per cent. All the present results are expressed for infinite dilution.

Let t and t' be the initial and final temperatures in any determination, where w grams of solution is mixed with W grams of water, the water equivalent of the apparatus being $w'c_1$ and the heat capacity of the resulting solution being c'', then, the heat developed by diluting

100 grams of the solution to the same extent as in the actual experiment (D^{100} observed) will be—

$$D^{100} = \frac{100[(W + w)c'' + w'c_1](t' - t)}{100}.$$

To reduce the values for D^{100} in the various mixing experiments to what they would be if the final strength of the solution was the same as in the last determination of the series, we must add to each the heat evolved on diluting the (about) 200 grams of weak solution obtained, with a further equal volume of water (determined in the next experiment), then that evolved on diluting the resulting (about) 400 grams to a similar extent, and so on, till the last stage of dilution is reached. These values are then plotted out, and the heat evolved on diluting the last solution with infinity of water is found, and the whole results recalculated with this as the zero point. Thus the heat of dissolution of any solution to infinity (D^{100}_{∞}), or even to a state of considerable dilution, depends not only on the actual determination with that solution, but on all the other determinations with weaker solutions increased in geometrical proportion. "The correction" for infinite dilution to be applied to the observed values in the case of sulphuric acid is particularly large: with an 18 per cent. solution it amounts to 656 cal., that is, twelve times the quantity measured (47 cal.) in the actual determination.

It is evident from this, how inadvisable it is to extend the mixing experiments to solutions of greater strength than is absolutely necessary.

With the dissolution experiments, the "correction to infinity" is relatively small, since the strength of the solution obtained in any determination is far less (2·5 to 0·25 per cent.) than in a mixing experiment; but even here it attains very large proportions, sometimes amounting to nearly 3000 cal., and sometimes exceeding the evolution measured in the determination itself. The correction* has to be deduced from the curve representing the results of the mixing experiments, very carefully enlarged in the manner indicated on p. 92.

The so-called "molecular" heat of dissolution is deduced from that of 100 grams by multiplying the latter by the molecular weight of the anhydrous substance, and dividing by the percentage composition of the solution.

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* $D^{100}_{\infty} = D^{100}$ obs. $+\left(D'^{100}_{\infty}\frac{W + w}{w}\right)$, in which D'^{100}_{∞} is the heat of dissolution of 100 grams of a solution of the strength of that resulting in the determination, and W and w the weights of water and strong solution taken respectively.

Experimental Error.

The average difference in the readings of the heat evolved as given by the two thermometers used together in the mixing calorimeter, was 0·0008°,* which would represent a difference of only 0·13 cal. in the two values for D^{100} in the one determination; but the values for D^{100}_{∞} would contain an accumulation of similar errors from all the determinations with weaker solutions, so that it is impossible to estimate the probable accuracy of these latter values, except by comparing them with the dissolution experiments (see below).

In the dissolution experiments, the average difference in the independent duplicates was found to be 7·6 cal. (in the corrected values for D^{100}_{∞}), so that the mean error of a single determination is 5·4 cal., and that of the mean of two determinations is 3·8 cal.,† the probable errors being two-thirds of these quantities. Two, and often three, determinations were made at each point.

This error is certainly very small, since an error of only 0·001° (0·1 mm. of the thermometric column) in the rise of temperature measured would, on the average, make a difference of 4·1 cal. in each result, and the errors entailed in the application of the large correction for dilution to infinity could not, from *a priori* considerations, be placed at less than double this value. Yet the smallness of the actual error is well established by some 150 determinations in the present case, and in other cases where the correction to infinity is smaller, and the weight of solutions taken can be larger, the mean error deduced from some 200 experiments is less than half the value here given.

Besides the magnitude of the "correction" and the small weights of strong acids which have to be taken,‡ there are other special sources of error in the present case, owing to the rise of temperature and, consequently, the rate of cooling being more than usually great, and owing to the tubes from which the acid has been emptied having to be weighed out on a delicate balance as well as may be, between the one minute intervals when the thermometer is read, and while, often, a drop of the hygroscopic acid is running down the outside of the tube.

In differentiation we depend on the relative accuracy of consecutive observations, and the error in comparing these would not, I think, be much greater than in comparing duplicate experiments with the same solution: the only cause (provided the compositions of the solutions are known correctly§) which could make it larger would be the different strengths of the final solutions, and, consequently, their different heat capacities, and the difference in the correction for infinity; but the quantities taken in duplicates generally differed so much, that there would often be a greater difference in final strength with the duplicates than with consecutive determinations. Such a difference in the quantities taken, though it increases the divergence of the duplicate results from the mean, tends to bring that mean nearer the true value.

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* Deduced from more determinations than the present paper contains.

† Varying from 6 to 2 cal. with the strength of the solution dealt with.

‡ To reduce the great rise of temperature.

§ Errors in the percentage composition of a magnitude such as are shown to be probable from the irregularities in the first differentials of the densities, would scarcely

Results obtained.

Of the two series of mixing experiments (Table XIV), the first and fuller one was, owing to the frequency of the changes exhibited with very weak solutions, alone available for extension so as to get the value for infinite dilution. A curve obtained by plotting out the values for $D^{100}_{\propto}/p$ was in this, and other cases, found more adapted for extension to 0 per cent. than the $D^{100}_{\propto}$ curve itself. In the calculation of the last determinations in both series, errors were subsequently discovered (indicated in the table), but, as the difference made by them was far within the limits of experimental error, it was not thought worth while to recalculate the results in consequence. The stronger solutions used in these experiments were made up independently of, and therefore had not quite the same composition as, the solutions obtained in the various preceding determinations; to apply the small corrections necessary on this account, the results had first to be calculated on the assumption that the two solutions in question had been identical (values given in the column headed $D^{100}_{\propto}$, approx.), the correction determined from the curve which these values formed, and then the various results recalculated.

Leaving these for the present, the dissolution experiments (Table XV) will be examined first.

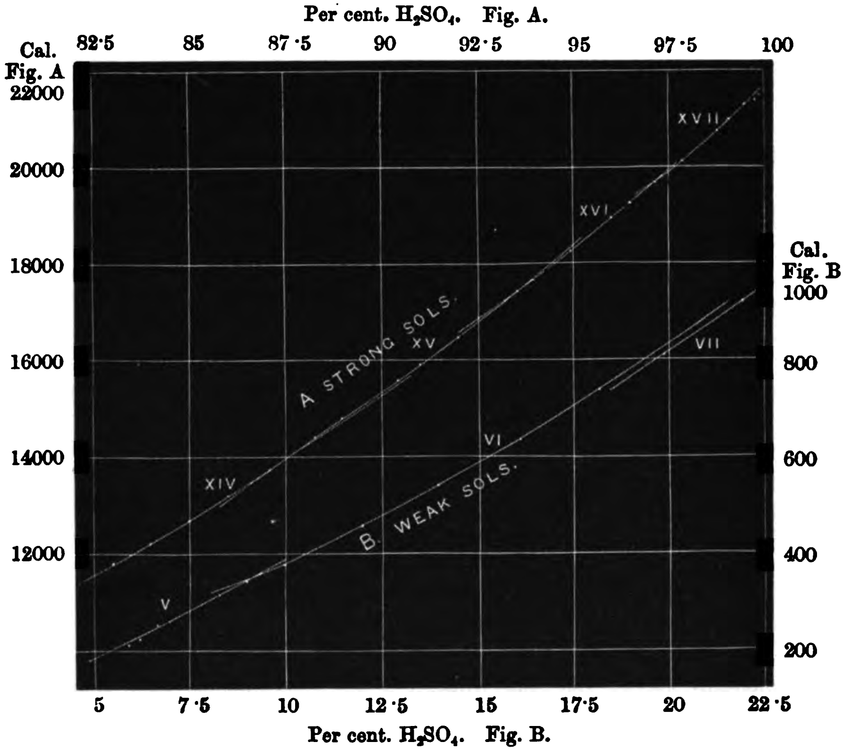
On a small scale they form a curve of great seeming regularity, very similar to that shown in Fig. 7, D (p. 97). The difficulty of treating them on a scale commensurate with the experimental error is considerable, owing to the rapidity of the increase and the magnitude of the quantities measured. They were generally treated in three overlapping portions, drawn to different scales, the total length of which was some 13 feet.

The two extreme portions of what I consider as being the smoothed curve representing these results are illustrated, though very imperfectly, by Fig. 8 (next page). The whole figure is continuous throughout,

have an appreciable effect on the heat of dissolution results, since the error thereby caused in the plotting of the results is partially counterbalanced by an opposite error introduced into the calculation of the magnitude to these results.

except in the vicinity of 20 and 50 per cent., where the discontinuity must, I think, be due to some error. Like the density curves, it can only be drawn in separate sections, but, unlike these, the sections all cut each other on prolongation. The average divergence of the experimental points (the means of two or three determinations) from the curve drawn was almost exactly what it should be, according to the estimate of the error deduced above from the difference between duplicates, and varied from 6·5 cal. with the stronger solutions (100 to 80 per cent.) down to 2·1 cal. with the weaker ones* (30 to 5 per cent.). There are, on the average, about six mean experimental points on each section. Of the various changes, that at 9 per cent.

FIG. 8.—Heat of Dissolution of Sulphuric Acid Solutions.



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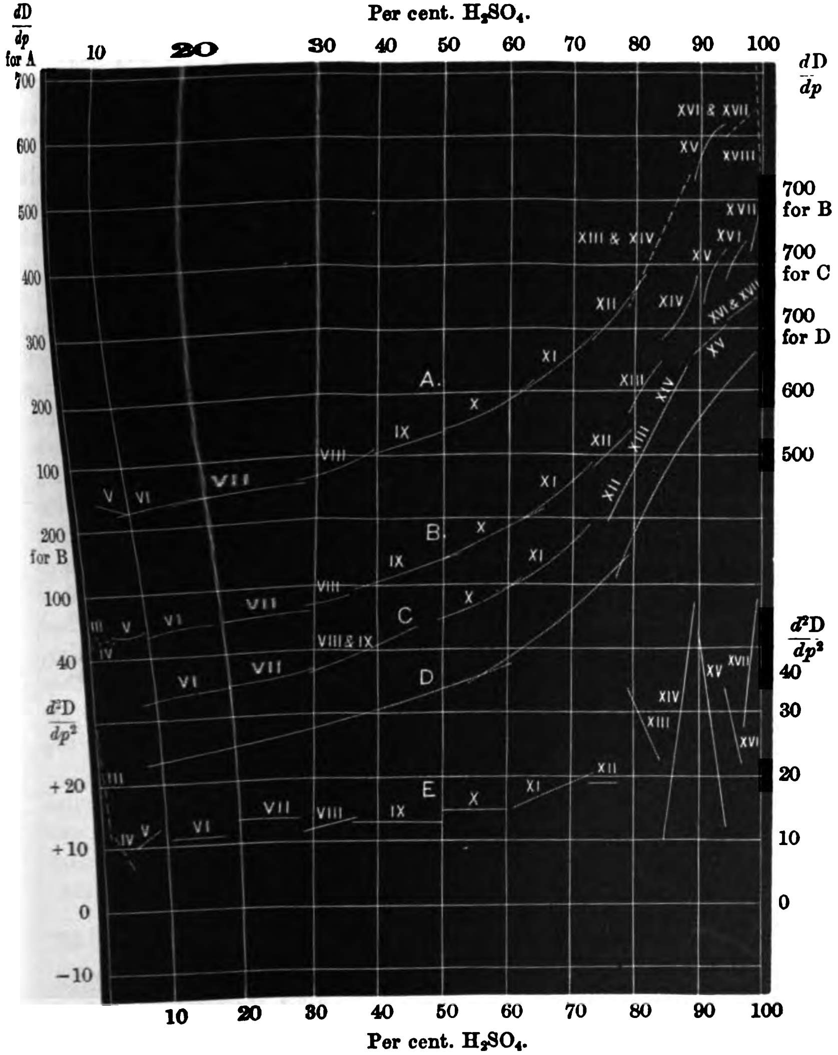
* Somewhat larger errors may be noticed in this and in other cases, where two solutions of nearly the same strength have been used. But in such instances the second determination was made owing to there having been some doubt as to the accuracy of the first: they would, therefore, lead to a wrong estimate of the average error.

is perhaps the most marked: some change at about 99·5 per cent. is established by the highest two points (containing six determinations), but these are insufficient to permit of any drawing being made of the curve on which they lie.

On differentiating this smoothed curve (Table XVI), the results

FIG. 9.—Heat of Dissolution of Sulphuric Acid Solutions. First Differentials and Second Differential.



illustrated by Fig. 9, B (p. 103) were obtained, each separate section of the original figure yielding either a curve, or a straight line, as a first differential. Two details may be mentioned:—(1) that a drawing of the original curve may be made, obliterating the change at 36 per cent., but that the differential from this drawing (given at the end of Table XVI) still shows a change here; (2) that no change at 84 or 73 per cent.—the composition of the mono- and di-hydrate—is noticeable in the experimental curve, and only becomes apparent after differentiation.

The first differential curve was then differentiated (Table XVI), and a discontinuous figure, which was rectilineal throughout, was thereby obtained (Fig. 9, E, p. 103). The comparative magnitude of the changes at the higher percentages is the chief point to be noticed respecting it.

On reconsidering these results, grave doubts were entertained as to the correctness of the conclusions drawn. It seemed possible that there might be some unknown sources of error in the experiments, and that the splitting up of the curve was but a consequence of the manner in which the figure had been drawn.

To settle this point, the results were again plotted out, but on a scale about half as open as before, and the curve was drawn without paying any attention to the position of the changes previously noticed, and purposely smoothing out all seeming irregularities. The only part which could not legitimately be smoothed over was the change at 9 per cent.; the curve therefore starts at this point. The readings of this curve will be found in Table XVII, and the differential deduced from them is illustrated by Fig. 9, C. It certainly offers ample justification for the interpretation given to the large scale drawing; for, in spite of the excessive smoothing, it still shows the majority of the changes which the latter had shown; their exact position has in some cases been slightly altered by the smoothing, and in four cases—namely, at 97·5,* 88,* 84, and 36 per cent.—they have been entirely obliterated, but the general agreement is far better than could have been expected. Table B, p. 109, gives the position of the changes shown by the two drawings.

The application of a direct differentiation to the experimental values proved a matter of great difficulty, and no success was obtained till the error was diminished by treating them in two series (last two columns of Table XV).† The result of this treatment, however, is to diminish the curvature of the constituent parts of the differential, and to obliterate two of the more feebly marked changes at 84* and 97·5 per cent. Fig. 9, A (p. 103) illustrates the figure thus obtained.† On applying a second differentiation to this (Table XVIII), a rectilineal figure was the result, closely resembling the second differential obtained from the smoothed experimental curve (Fig. 9, E), except in the parts between 80 and 88 per cent., and between 94 and 100 per cent., where the nature of the first differential was uncertain, and the straight lines here drawn to represent it gave two horizontal lines on the second differentiation. No illustration of this second differential is here given.

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* Of these two, however, there were some indications; those at 84 and 36 per cent. were very feebly marked even in the large curve.

† See footnote, p. 74; there are here so many pairs of differential points deduced from determinations with solutions of nearly the same strength, that I have marked them A and A′, &c.; A being a differential deduced from two deter-

The remaining drawing, D, in Fig. 9, is worthy of special attention. It shows the results of pushing the smoothing process still further than was done in what I have termed the ultra-smoothed curve, which gave the differential, Fig. 9, C. If, instead of taking readings from the ultra-smoothed experimental curve at every 1 or 2 per cent., we take them at considerable distances, say, at every 5 per cent., greater smoothing will be produced in the differential obtained from them; but, though the majority of the changes are thereby obliterated, the magnitudes of those near certain points are intensified, and we get Fig. 9, D, which cannot be drawn except as three distinct curves, one of which bends in the opposite direction to the other two.

The mixing and dissolution experiments have to be treated separately, for, where they overlap (5 to 18 per cent.), there is a considerable difference between them. This difference reaches as much as 16 cal., but, as it would be caused by a single error of 0·06 cal. or 0·0003° in the experiment with the weakest solution (0·08 per cent.)—supposing all the other determinations to be absolutely correct—it must be considered to show a remarkable degree of concordance.‡

In dealing with these mixing experiments, the rapid increase in the heat evolved renders it necessary to plot them out to several different scales. The most extensive of these is illustrated by

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minations marked A, and A′ being one from one determination marked A and one marked A′.

* The irregularity of the points near this percentage indicated the probability of some change. But there were not enough points to define it.

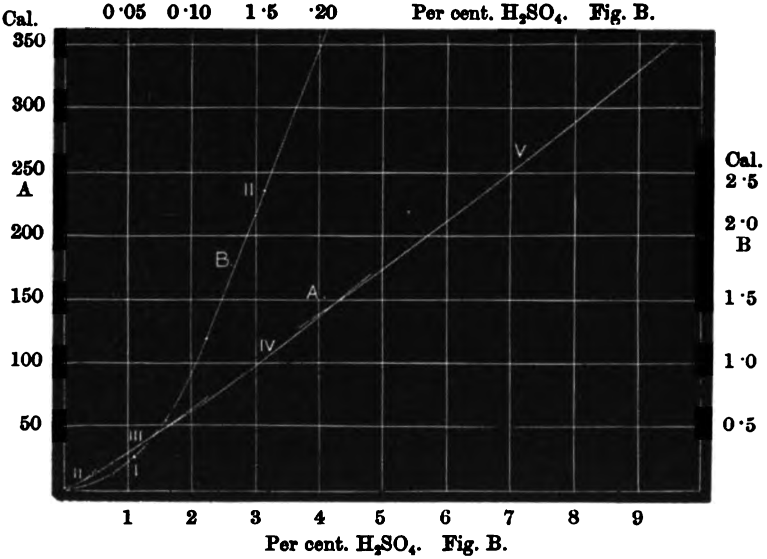
† The line XVIII is, of course, not established, and is only of use in showing the existence of a change above 99 per cent. The drawings of the various smoothed experimental curves do not extend beyond this percentage.

‡ Better concordance might be obtained by re-calculating the mixing experiments, starting with the strongest solution and working downwards, instead of starting with the weakest solution and working upwards, as in the first case. The actual value to be taken for the strongest solution would have to be deduced from the results of the dissolution experiments, a considerable number of these being performed at the point in question.

Fig. 10, A :* the changes which occur in it, of which the best marked one is at 4 per cent., are of the same character as those in the region of stronger solutions. The general change in direction at the extreme end is very remarkable: it is illustrated on an enlarged scale in Fig. 10, B. The curve here is of such a nature that it cannot be drawn conveniently with a bent ruler; and more satisfactory results were obtained by plotting out the values for D^{100}_{∞}/p, as shown in Fig. 11.

FIG. 10.—Heat of Dissolution of Sulphuric Acid Solutions.

Mixing Experiments.



This figure is well worthy of attention. The results of the second series of experiments are distinguished from the others by crosses; the point at 0·88 per cent. appears to be somewhat anomalous; but, whether we include it or omit it (as has here been done in making the present drawing), it will be apparent that the inclination of the curve becomes very abrupt somewhere about 0·4 per cent.,† and that

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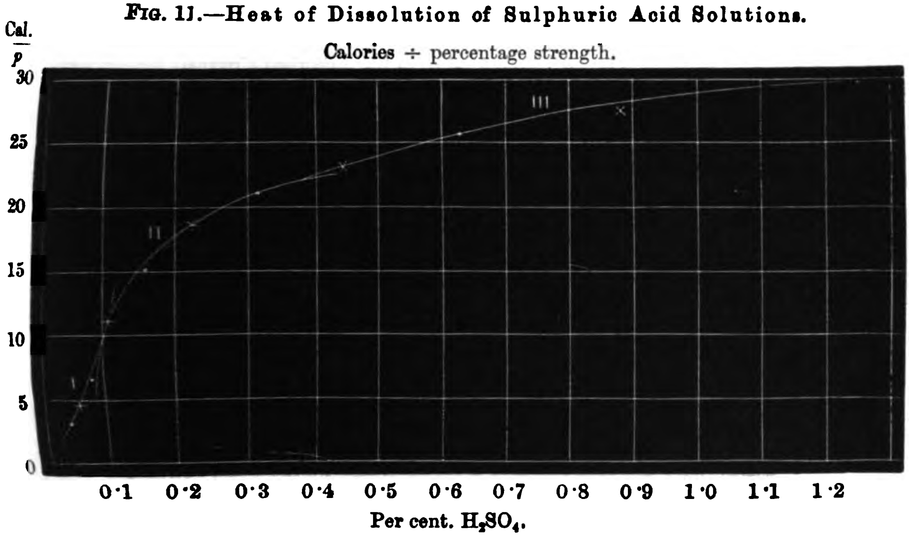
* The highest determination, that at 18 per cent., is too far from the next lower one (9 per cent.) to be of any service in drawing the curves.

† It may be here noted that this remarkable change could not have been revealed by Thomsen's determinations, since his results ended with a 0·34 per cent. solution. The importance of extending any series of determinations to the greatest dilution possible is rendered very evident by the present results.

There are two slightly different drawings of this curve below 0·16 per cent.; both are treated in Table XX.

FIG. 11.—Heat of Dissolution of Sulphuric Acid Solutions.



about 0·1 per cent. it alters its direction again, bending in the opposite direction.

If this form of plotting the results be extended to stronger solutions, the curve again bends upwards, presenting on the whole the same general appearance as Fig. 7, E (p. 97), the values for D_{α}^{100}/p being of the same nature as those for the so-called molecular heat of dissolution.

The differentiation of the mixing experiment curve (Table XIX)* is illustrated in Fig. 12 (next page). The first differential, A, is composed of well-marked curves; whilst the second one, B, is rectilineal within experimental error. The comparative magnitude of the changes with very weak solutions may be judged by the portions III and IV, which are reproduced as dotted lines in Fig. 9, B and E. On a larger scale, a certain amount of curvature in the second differential line I is noticeable, but this is probably due to error. A difference in the nature of the curvature of line V in the first differential, as shown by the mixing or dissolution experiments, will also be noticed, and is no doubt due to the rapid accumulation of small errors in the former.

The number of changes which existed with weak solutions showed that it would be useless to perform a direct differentiation of the experimental values, owing to the comparative paucity of the determinations.

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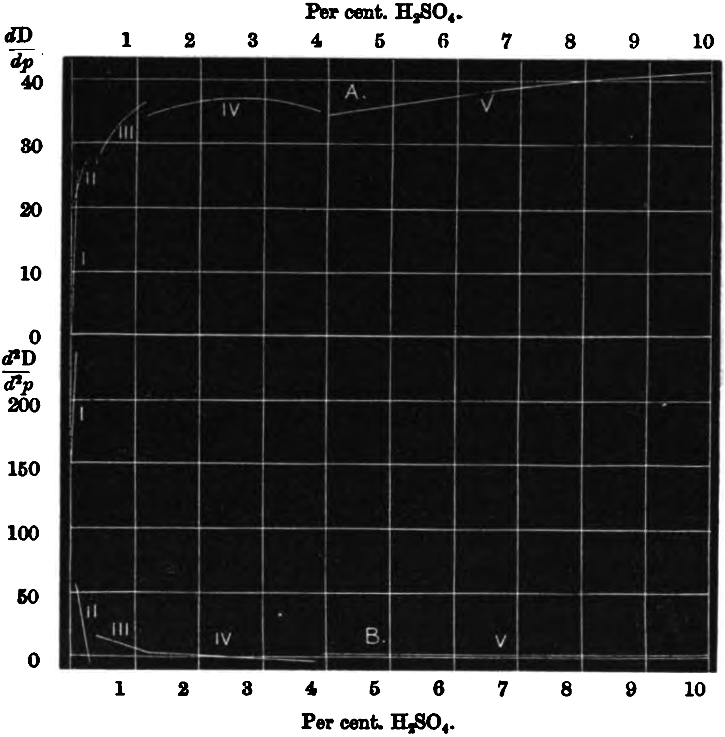
* The values for the weakest solution were deduced from readings of the D_{α}^{100}/p curve.

FIG. 12.—Heat of Dissolution of Sulphuric Acid Solutions.

First and Second Differential from the Smoothed Curves.



The positions of the various changes shown by the heat of dissolution results are collected in the following table, B. The ultra-smoothed curve gives approximations only: the results obtained from an examination of the smoothed experimental curve (together, sometimes, with that of the first differential deduced from it) are more trustworthy than those from the direct first differential. The mean does not include the values in the first column.

The concordance of the position of the changes, as determined by the two methods of analysis, is very good; yet, the heat results generally cannot be regarded as very satisfactory when considered by themselves, and, looking at the number of determinations which were made, and the care which was taken about them, they proved somewhat disappointing.

Perhaps such a result should have been anticipated, owing to the thermometer being an instrument 50—100 times less delicate than

TABLE B.—*Position of the Changes in the Heat of Dissolution Curves.*

From the 1st diff. of the ultra-smoothed curve (approximate).	From the smoothed curve.	From the direct 1st diff. curve.	Mean.
—	99·5	99·2[†]	99·35
Possibly 97·5	97·3	—	97·3
94	93·5	93·8	93·83
87	88·9	89·0	88·95
—	84·0	—	84·0
76[*]	79·0	79·0	79·0
	73·0	73·0	73·0
61	58·3	60·0	59·15
49	49·5	49·0	49·25
—	35·5	39·0	37·75
28	28·0	28·5	28·25
20	19·3	19·0	19·15
9·5	8·7	9·3	9·0
	4·07		4·07
	1·13		1·13
	0·40		0·40
	0·11		0·11

the balance on which the densities depend, and to the fact that the results of the individual determinations cannot be utilised directly, as the densities can, without the application of complicated calculations and corrections. Many of the changes are so feebly marked that much uncertainty must prevail as to their existence and position; it was only by the expenditure of an amount of time and trouble, of which the present account can give but a faint idea, that any definite conclusions could be arrived at. It is not difficult to see the reason of this. The magnitude of the individual changes appears to bear no relation to the magnitude of the total heat evolved, or to the rapidity with which this increases with the strength of the solution. These last two peculiarities of the reaction have the sole effect of rendering the experimental error almost double what it would be in any ordinary case, and of necessitating the adoption of methods (differentiation in alternate series) which tend to obliterate the sharpness with which the changes of curvature are marked.

Table C (p. 110) contains the values for the so-called molecular heat of dissolution (D^{m}_{∞}). The strengths entered are either such as correspond to the hydrates which exist according to the present work, or such as will permit of a comparison of my own determinations with those of Thomsen and Pfaundler (*Thermochem. Untersuch.*, 3, 54, and

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[*] Very uncertain. There might be a change on each side near 76 per cent., instead of one at 76 per cent.

[†] Probably rather higher.

TABLE C.—*Molecular Heat of Dissolution* (D_{α}^{m}) *of Sulphuric Acid Solutions at* 17·91°.

Composition.		Molecular Weight.	D_{α}^{100}.	D_{α}^{m}.		
Molecular.	Per cent. H_2SO_4.			Pickering.	Pfaundler.	Thomsen.
H_2SO_4	100	97·82	21563	21093	21165	19981
H_2SO_4, $\frac{1}{36}H_2O$	99·473	98·32	21215	20858	—	—
„ $\frac{1}{6}$ „	97·030	100·81	19627	19787	—	—
„ $\frac{1}{3}$ „	94·233	103·81	17885	18566	—	—
„ $\frac{1}{2}$ „	91·592	106·80	16280	17387	17395	—
„ $\frac{2}{3}$ „	89·095	109·79	14840	16293	—	—
„ 1 „	84·488	115·78	12460	14426	14332	13602
„ $\frac{3}{2}$ „	78·407	124·76	9995	12470	—	—
„ 2 „	73·142	133·74	8363	11187	—	10563
„ 3 „	64·483	151·70	6193	9395	9518	8844
„ 4 „	57·656	169·66	4828	8191	8255	—
„ 5 „	52·137	187·62	3918	7851	7367	6873
„ $5\frac{1}{2}$ „	49·757	196·60	3552	6983	—	—
„ 6 „	47·582	205·58	3252	6686	6652	—
„ 9 „	37·701	259·46	2088	5418	—	5029
„ 13 „	29·526	331·30	1399	4635	—	—
„ 19 „	22·279	439·06	941	4132	—	3725
„ 24 „	18·492	528·86	748	3957	—	—
„ 49 „	10·003	977·86	381·5	3732	—	3297
„ 58 „	8·585	1139·5	330*d* 313*m*	3760*d* 3566*m*	—	—
„ 99 „	5·215	1875·9	188·5*d* 182·9*m*	3536*d* 3431*m*	—	—

(*d*) From "dissolution" experiments, (*m*) From "mixing" experiments.

TABLE C—*continued.*

Composition.		Molecular Weight.	D_{α}^{100}.	D_{α}^{m}.		
Molecular.	Per cent. H_2SO_4.			Pickering.	Pfaundler.	Thomsen.
H_2SO_4, $119H_2O$	4·377	2235·1	161·0*d* 152·7*m*	3598*d* 3411*m*	(3411)	—
,, 130 ,,	4·021	2432·6	147·7*d* 138·5*m*	3593*d* 3373*m*	—	—
,, 199 ,,	2·664	3671·9	93·8	3445	—	2916
,, 399 ,,	1·346	7265·9	41·55	3020	—	2668
,, 510 ,,	1·057	9257·2	30·6	2833	—	—
,, 799 ,,	0·677	14448	17·54	2533	—	2340
,, 1500 ,,	0·362	27038	8·00	2163	—	—
,, 1599 ,,	0·340	28816	7·37	2124	—	(2124)
,, 5200 ,,	0·104	93490	1·085	1021	—	—
,, 8000 ,,	0·068	143778	0·403	58	—	—

(*d*) From "dissolution" experiments. (*m*) From "mixing" experiments.

If the composition of the acid as given by the freezing point determinations be taken, the above values will be somewhat too high; that for D_{α}^{100} for 100 per cent. will be 50 cal. too high, that for a 50 per cent. solution, 18 cal. too high, and the others in like proportion.

TABLE D.—*Heat Evolved on Addition of Various Proportions of Water to Sulphuric Acid Solutions at* 17·91°.

$H_2SO_4mH_2O,\ nH_2O$.

m.	*n.*	Pickering.	Pfaundler.	Thomsen.	Cal. per mol. H_2O added. (Pickering.)
0	1	6667	6833	6379	6667
1	1	3239	—	3039	3239
2	1	1792	—	1719	1792
3	1	1204	1263	—	1204
4	1	840	888	—	840
5	1	665	715	—	665
5	4	1933	—	1844	484
9	10	1286	—	1304	129
19	5	175	—	—	35·0
49	50	196*d*	—	174	3·9
99	100	−14*m*	—	207	−0·14
199	200	425	—	248	2·13
399	400	487	—	328	1·22
799	800	409	—	216	0·51
0	$\frac{1}{6}$	1306	—	—	7836
$\frac{1}{6}$	$\frac{1}{6}$	1221	—	—	6326
$\frac{1}{3}$	$\frac{1}{3}$	2272	—	—	6716
$\frac{2}{3}$	$\frac{1}{3}$	1867	—	—	5601
1	$\frac{1}{2}$	1956	—	—	3912
$\frac{3}{2}$	$\frac{1}{2}$	1283	—	—	2566
510	990	670	—	—	0·677
1500	3700	1142	—	—	0·308
0	$\frac{1}{2}$	2706	2770	—	5540
0	1	6667	6833	6379	6667
0	2	9906	—	9418	4953
0	3	11698	11647	11137	3899
0	4	12902	12910	—	3225
0	5	13742	13798	13108	2748
0	6	14407	14513	14952	2401
0	9	15675	—	—	1742
0	19	16916	—	16256	890
0	49	17361	—	16684	248
0	99	17557*d* 17662*m*	—	16858	174
0	199	17648	—	17065	89·7
0	399	18073	—	17313	45·5
0	799	18560	—	17641	23·2
0	1599	18967	—	17857	11·8

Jahresb., 1869, 122). Table D gives the values for the heat evolved on adding various proportions, and also successive proportions, of water to the strong acid. Where there might be a doubt as to whether the values were deduced from the mixing or dissolution experiment, the letters *m* and *d* have been inserted.

The error in these absolute values is, of course, very different from that of the relative values of successive determinations, which has heretofore been alone considered. A difference of 0·001° or 0·2 cal. in the determination of the value for a 0·4 per cent. solution would make a difference of 50 cal. in the heat of dissolution of H_2SO_4 itself;* yet the concordance of the mixing and dissolution experiments showed that the actual error accumulated as far as 18 per cent. could not have amounted to more than one-seventh of this, so that the value for H_2SO_4, is, in all probability, right considerably within 50 cal. To compare my values with Thomsen's and Pfaundler's, these latter must all be increased by 2124 and 3411 cal. respectively, the heats of dissolution of the weakest solutions (0·34 and 4·377 per cent.) which these two physicists obtained in their final experiments. Pfaundler's values, it will be seen, agree very satisfactorily with my own, there being but one instance in which the difference between our results exceeds 100 cal., whereas Thomsen's results are all considerably lower, the difference amounting to as much as 1112 cal. in the case of the pure acid. This difference, I imagine, may be caused by errors due to Thomsen's mixing calorimeter, or to the acid which he used not being as strong as H_2SO_4.†

It will be seen by the footnote at the bottom of Table C (p. 111) that my values are probably somewhat high, but the excess would be almost exactly counterbalanced by taking 98 instead of 97·82, as I have done, for the molecular weight of H_2SO_4: Pfaundler and Thomsen took the former of these values.

The manner in which the results are stated in Table D does not show the discrepancy between Thomsen's results and those of Pfaundler and myself so forcibly. A considerable difference will be noticed, however, in the case of $H_2SO_4 799H_2O$, $800H_2O$—Thomsen's last determination. There is certainly, I think, an error here, and it will affect all his values for D^m_∞ (see Trans., 1889, 325).

It will be seen from the upper portion of the last column of Table D that the heat evolved for H_2O, on the addition of successive portions of water, diminishes till $199H_2O$ have been added, that it then increases, and again diminishes. From the last portion of this column it will also be seen that the heat evolved on adding the first

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* If it were determined by mixing the acid with consecutively *equal* volumes of water, as in the "mixing" experiments, the error of 0·2 cal. at 0·4 per cent. would make an error of 500 cal. in the value for H_2SO_4.

† He says nothing about the preparation or analysis of it, and his values are such as would be obtained with a commercially "pure" acid of 97—98 per cent. Pfaundler took pains to prepare his acid by crystallisation.

$\frac{1}{2}$ mol. of water to H_2SO_4 is considerably less, instead of greater, than that evolved on the addition of the second $\frac{1}{2}H_2O$, as it should be if the curve were regular throughout. Thus there are at least two portions of the curve which, even on a cursory inspection, show that it does not possess that general regularity which the supporters of the physical theory of solution are so anxious to attribute to it.

PART VI.—EXPANSION BY HEAT.

A. *As a Function of Percentage Composition.*

The density determinations made, supply the means of calculating the expansion of the solutions by heat. In doing so we depend on the comparison of two series of results at *different* temperatures, and, hence, the conclusions drawn may be regarded as almost independent of those already drawn from the densities themselves, where we depended on the results of one series at the *same* temperature.

If s_1 and s_2 be the densities at t_1 and t_2, the expansion, or increase in volume, will be $\frac{s_1}{s_2} - 1$, the volume at the lower temperature t_1 being taken as unity. In this way I have calculated the expansion in several cases, but have preferred to take, for the purposes of analysis, the complementary property of the decrease of density, $s_1 - s_2$*: the figures in the two cases are of a similar nature, but the latter present the advantages of (1) an error in the densities causing an error of the same magnitude throughout; (2) an error in the density determinations having generally a smaller effect (actual and relative) on the results; (3) of necessitating fewer calculations, and possibilities of mistakes.

The solutions used at 17·925° had not the same composition as those used at the other temperatures, so that, if we take the actual experimental values, we can only get the expansion for about 10°, from 28·064° to 38·203°; for about 20°, from 7·978° to 28·064°; and for about 30°, from 7·978° to 38·203°. These values are given in Table XX.

To utilise the results at 17·925°, the values, as reduced to round percentages (and also to whole degrees of temperature), given in Tables VII and VIIA, must be taken. From these we get three series for a rise of 10°, two for a rise of 20°, and one for a rise of 30°; they are given in Table XXI, and will probably yield more uniform results than those derived from the unreduced densities, since, in the reduction, a few obvious errors were corrected (see p. 70).

In the case of the numerous results with strong solutions, and for results below 20 per cent., the reduced densities at 8° and 18° are alone sufficiently trustworthy for the present purposes. Table XXI also contains the values for the expansion proper for the three 10° intervals.

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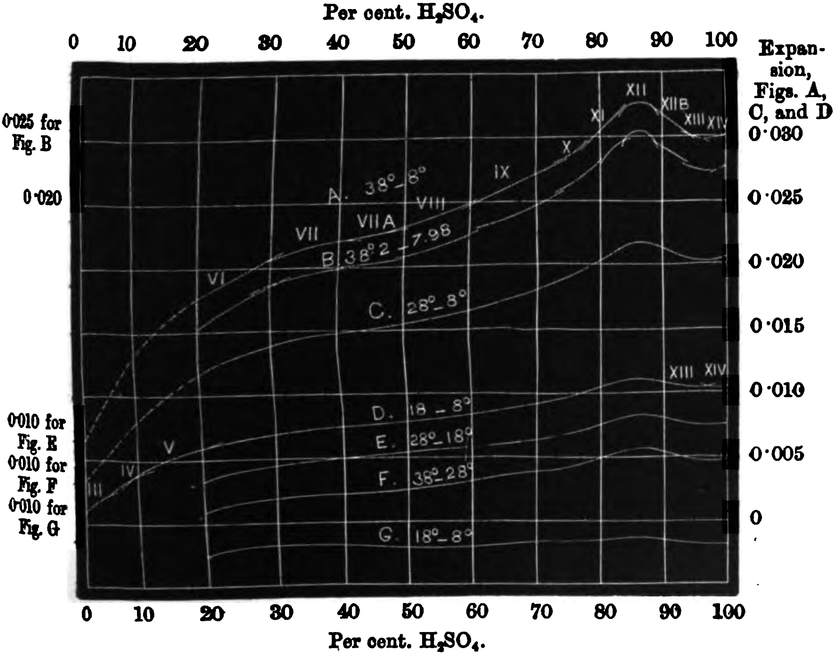
* This divided by the density at the higher temperature gives the expansion.

Fig. 13 gives a representation of some of the results obtained, the signs of the values for the decrease in density having been changed to +, so that the figures may be more easily compared with those for the expansion proper. A, C, and D give the decrease in density for intervals of 30°, 20°, and 10°, deduced from the reduced values; E and F (which should be raised $\frac{1}{2}$ and 1 division of the paper respectively), the values for the other intervals of 10°; G (which should be raised $1\frac{1}{2}$ div. of the paper) shows the expansion proper for 10°; and B (which should be raised $\frac{1}{2}$ div.) gives the decrease in density for the 30° interval as deduced from the unreduced density values.

FIG. 13.—Decrease of Density, and Expansion of Sulphuric Acid Solutions on being heated 30°, 20°, and 10°.



All the figures resemble the first differential of the densities in being continuous throughout,* and yet necessitating their being drawn in sections, when a bent ruler is used for that purpose. The separate sections are indicated in the present illustration in the cases of A, B, and the end portions of D only.*

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* Except in some parts of B, where the discontinuity is probably the result of errors.

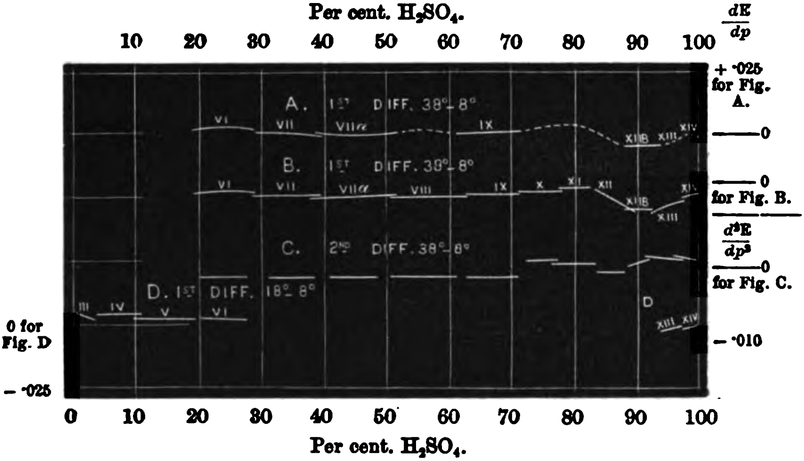
The agreement of the experimental points with these drawings is somewhat better than in the case of the first differential of the densities (Plates 1 and 2, p. 184) when the same scales are used.

Both as regards the position of the changes and the nature of the constituent curves, the various figures resemble each other so closely, that I have analysed by differentiation that only which refers to the 30° interval, supplementing it in the case of very strong and weak solutions by a similar examination of Fig. D.

The direct differentiation (Table XXI, and Fig. 14, A) gives a figure composed of three straight and two slightly curved lines, there being three parts of it in which the results are too doubtful to permit of any drawing being made. Indeed, it could hardly be expected that the decrease in densities would stand a direct differentiation, for the original values here are merely the differences between two experimental results and, even in the case of the 30° interval, they are only comparable in accuracy with the first differential of the densities.

FIG. 14.—Expansion of Sulphuric Acid Solutions.

First and Second Differentials.



A differentiation of the smoothed curve (Fig. 13, A, p. 115) led to better results (Table XXII and Fig. 14, B), and supplied sufficient data for the drawing of those parts where the direct differentiation had failed. The whole of the figure from 50 to 88 per cent. is rectilinear, the other portions of it being made up of gentle curves. A second differentiation (Table XXII) reduces all these curves to straight lines, and gives the figure illustrated by C, Fig. 14. There are, of course, non-comformable points between most of the lines constituting this figure.

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* In plotting out the results from the unreduced densities, considerable assistance may be derived from a study of Plates 1 and 2, which will indicate which determinations probably contain exceptionally large errors.

The first differential of the curve for the 10° interval for weak and strong solutions will be seen from Fig. 14, D, to be made up of sundry straight lines: the portion III does not appear to apply quite as far as 0 per cent., the last few points in the diagram exhibiting an irregularity, which indicates the occurrence of some change at 0·3 to 0·4 per cent.; but this is simply a suggestion.

Table E (p. 118) summarises the information as to the position of the changes derived from a study of the various results. The numbers given at the bottom of the columns refer to the weight which has been assigned to the figures in that column in deducing the mean: the weighting has been made in proportion to the interval of temperature to which the expansion applies: the results drawn from a direct differentiation, the differentiation of the smoothed curve, and also from the inspection of the original curve, count as independent observations, so that the value attached to the results from that curve in which the changes have been established by differentiation may amount to two-thirds of that attributed to the evidence derived from a mere inspection of all the other curves together. This is the only instance in which I have attributed any weight at all to conclusions drawn from an experimental diagram, without confirming the changes shown in it by differentiation. Such changes as are specially doubtful are enclosed in brackets, and to these only half the value of the other points has been attributed.

The general concordance of the results is certainly satisfactory. Very little weight can be (and is) attached to the indications between 89 and 50 per cent. for the 10° intervals. Nearly all the results suggest a change somewhere about 62 per cent., where none of the other properties studied have shown one; this is very probably due to the results in this neighbourhood being affected by some error in the composition of one or two of the solutions (p. 76). Due, probably, to the same cause, we have the fact that a change at 57 per cent. is unmarked in most of these results, although it has been established by nearly all the other properties investigated. It is to be noticed that a change at 89 per cent. is well established by all these results, although of the density results, that at the lowest temperature was the only series which indicated it.

There are several points of interest besides the position of the changes.

TABLE E.—*Position of the Changes shown by the Curves for the Expansion of Solutions by Heat.*

From the unreduced values.			From the reduced values.									Mean.
8—38° curve.	8—28° curve.	28—38° curve.	8—38°.			8—28° curve.	18—38° curve.	8—18°.		18—28° curve.	28—38° curve.	
			Curve.	Direct 1st diff.	1st diff. from curve.			Curve.	1st diff. from curve.			
(98)	—	(98)	97	(97)	—	97	(98·5)	97·5	97·5	—	—	97·38
94	94	94	94	94	93·3	94	94	—	—	94	94	93·91
89	89	88·6	88·8	88·5	89	87·6	88	(89)	—	(89)	89	88·71
84·5	84·5	—	83	—	83	83·1	84·5	(82·9)	—	—	84	83·43
(80·5)	79	(80·5)	78	—	78	78·2	78·9	(77)	—	79	—	78·63
73	72	73	72·6	73	73	72·6	72·6	73	—	(74)	(73)	72·79
(62)	(61)	(62)	62	(61)	62	(63)	(63)	(59)	—	(63·6)	62	(61·92)
—	—	—	—	—	—	57	56·4	—	—	—	(57)	(56·73)
49	—	—	48	(50)	50	48·4	—	49	—	50	—	49·09
39	41	(41)	39·4	38	38	39	40·5	38·5	—	(40)	39·5	39·18
28·6	28·4	(28·8	29	28	29	28·5	29	29	—	30	28·5	28·83
—	—	—	—	—	—	—	—	20	19	—	—	19·50
—	—	—	—	—	—	—	—	11	10	—	—	10·50
—	—	—	—	—	—	—	—	4	4	—	—	4·00
—	—	—	—	—	—	—	—	(·35)	—	—	—	(0·35)
6	4	2	6	6	6	4	4	2	2	2	2	—

The values in this Table refer to percentages expressed according to the results of the freezing point of the acid, and are 7/10,000ths higher than in any preceding Table.

The three 10° curves, when compared together, show that the effect of temperature on this property is largely dependent on the composition of the solution taken. At about 57 per cent. the expansion from 8° to 18° (Fig. 13, D, p. 115) shows a depression, whereas that from 18° to 28° (E) shows an elevation, and that from 28°—38° (F) shows a uniform increase, so that from 8° to 38° the rate of expansion of this solution will increase with the temperature.* With a solution of about 70 per cent. strength, the reverse will be the case. All the peculiarities exhibited by these three curves are equally shown by the corresponding curves representing the expansion proper, one of which is illustrated by Fig. 13, G.

There is a well-marked maximum of expansion, which in all cases appears to be situated at 86·3 per cent.; a percentage, be it specially noted, which corresponds with no definite hydrate, and with no sudden change in the curve.

The comparatively high points shown by the difference of density at about 33 per cent. become points of maxima in the expansion proper. The position of this second maximum is not so clearly defined as that of the first, and appears to vary somewhat with the actual temperature. From 8° to 18° it is situated at about 33 per cent., from 18° to 28° at 34 per cent., from 28° to 38° at 32°; but these variations are very doubtful. In any case it is not situated at a point corresponding to any abrupt change in curvature. With the expansion from 18° to 28°, there is, further, a slightly marked maximum at about 57 per cent. It may also be noticed that the change at the monohydrate (84·5 per cent.) is very feebly marked in the original curve, and becomes pronounced only when we come to the first differential.

That the constituent curves of the figure representing the expansion require two differentiations in some cases is, I think, fairly certain, especially when it is remembered that the small magnitude of the original quantities dealt with would favour their differentiation into practically straight lines, and that, in spite of this, six out of the eleven portions constituting the first differential (Fig. 14, B) exhibit a decided curvature. These constituent curves do not appear to meet tangentially, and, consequently, the straight lines forming the second differential do not meet at the points of change.

B. *As a Function of the Temperature.*

The above results have shown that the expansion is sometimes greater and sometimes less as the temperature is higher, according to the strength of the solution. A few determinations were made with a view of gaining further information on this point.

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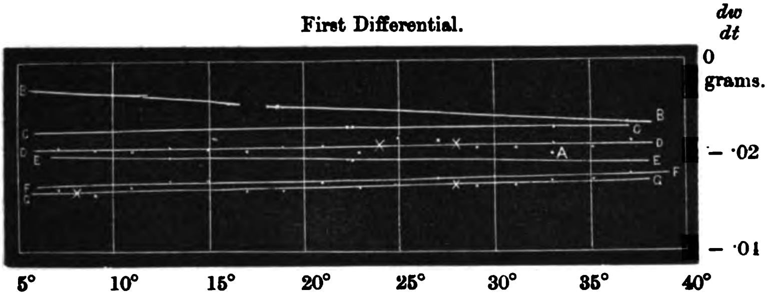
* These features are barely visible in the rough sketch given in Fig. 13.

Three solutions, containing 84, 81·1, and 41·8 per cent. of acid respectively, were taken, and their densities determined at every 2° between 6° and 38°. The first of these solutions has a composition nearly corresponding with that of the monohydrate, the composition of the second coincides with no particular hydrate, and the third solution was taken simply at random, as an instance of a weaker solution. Table XXIII embodies the results.

The weights of the contents of the bottle, when differentiated, give the figures in Fig. 15.* The scale is somewhat too open for the experimental error (which here depends on the correctness of the actual temperatures as well as on the weighings), and the points for the 81·1 per cent. solution have not been inserted: the crosses represent the mean points given in the table. The three lines are all continuous and straight within the errors of the experiments, from which it would follow that the change of the density with temperature is represented in each case by a single parabola of the second order† as far as the determinations extended.

Fig. 15.—Weights of Water and Acid contained in a 25 c.c. bottle at $t°$.


First Differential.

B = water.
C = 20 per cent. acid.
D = 41·8 „ „
E = 60 „ „
F = 81·1 „ „
G = 84 „ „

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* Differentiation of the densities or volumes would give lines differing only in position and inclination (not in form) from those derived from the weights; but they would contain the errors due to the determination of the capacity of the bottle at each temperature.

† Mendeléeff drew the same conclusions from his determinations with alcohol solutions between 0° and 30°. The points determined with each solution, however, never exceeded five.

That this, however, is not the case with all solutions, there are theoretical considerations (given below), as well as direct evidence, to show. In constructing the table of densities of solutions of the acid, the four results with each solution were plotted against temperature, and it was found that, whilst with all solutions of 100 to 63, and from 43 to 20 per cent., the results lay in an apparently uniform curve, from 63 to 43 per cent. they could only be depicted by two different curves bending in opposite directions, or by two different straight lines* (the latter with solutions from 53 to 43 per cent.). This indicates the existence of more or less abrupt changes at certain temperatures with some solutions, and the instances found were too numerous and consistent, and the differences too great (sometimes 0·0006 of the density, or 0·76°) to admit of their being explained away by experimental error. The differential obtained in one of these cases (for a 60 per cent. solution) is given in Fig. 15, E; the three points, of which A is one, cannot be represented by the same straight line, the error here being but one-fifth of what it is with the lines for 84, 81, and 42 per cent. solutions: an instance is also given in the figure of the differential obtained from a case (20 per cent.) where the four experimental points lay on one curve, and here we get an uniform straight line.†

It was certainly unfortunate that the solutions selected for the fuller examination of the effect of temperature on density should not have included any in that region where the effect was subsequently found to be irregular.

The different inclinations of the various lines in Fig. 15 confirm the previous conclusion that the rate of expansion is sometimes greater, and sometimes less, at the higher temperature, according to the strength of the solution examined.

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* Or a curve and a straight line.

† The actual values in these two cases are:—

60 per cent.				20 per cent.			
t°.	s.	w.	$\frac{dw}{dt}$.	s.	w.	$\frac{dw}{dt}$.	t°.
7·978	1·506415	37·7079	·0201	1·146050	28·6874	·0141	12·95
17·925	1·498077	37·5078	·0204	1·140179	28·5469	·0142	22·99
28·064	1·489582	37·3010	·0193	1·134250	28·4031	·0144	33·13
38·203	1·481526	37·1055		1·128243	28·2575		

PART VII.—DISCUSSION OF THE RESULTS.

The persistency with which the methods here adopted for examining curves has been misunderstood,* renders it necessary for me to say a few words on the subject, even at the risk of repeating myself.

The method does *not* consist in fitting sundry equations on to the curves, and, on the strength of the concordance observed, to conclude that these latter are continuous or otherwise. It is quite true that if a curve differentiates into a straight line after a certain number of differentiations, an equation of a certain form must represent that curve, and, if it yield several straight lines, there must be as many different equations applicable to different parts of it; but it is one thing to find equations empirically, and prove (?) their truth by a display of those, often, most fallacious of arguments known as tables of "found" and "calculated" values, and another thing to apply an ordinary process of mathematical analysis to them, letting them speak for themselves, and tell us whether they are continuous or not. On the former of these methods I would place absolutely no reliance, and so far have I been from making use of it, that I have not found the equation for any single curve here depicted.

The mathematical argument on which the method depends is that a curve, if it be continuous, will, on differentiation, give either a straight line or another continuous curve; whereas, if it be not continuous, but be made up of different curves, it will yield a series of straight lines or curves. This, I think, is an incontestable fact.

Of the dangers attending differentiation, and the consequent uncertainty of any conclusions depending entirely on this process, I have already said enough, and it is only necessary to remind my readers here that the recognition of the changes of curvature rarely depends on differentiation only, but that these are generally noticeable in the experimental curves themselves. On the other hand, it must be admitted that conclusions drawn solely from the experimental curves would be equally unsatisfactory; they would be dependent on the taste of the draughtsman, and on the drawing of a particular portion of a figure in one section—which, without the subsequent evidence supplied by differentiation, would be no proof that the section drawn is a single curve—but in no case have such unsupported conclusions been drawn.

In some instances, of course, the experimental curves might show changes of such abruptness that a mere cursory inspection would be sufficient to prove their existence, but it would be highly improbable that any of the properties here studied would do so; these properties must be continuous functions of the percentage composition, and, whatever changes they show, will be of a somewhat uncertain nature, since they must be due to changes in the unstable and dissociating liquid hydrates present.

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* See *Nature*, **40**, 343.

The main point of my opponent's attack will, I imagine, be directed against the closeness with which my drawings follow the experimental values. That I have ever gone within the limits of known or probable errors, I must deny, and I have often left a considerable margin beyond these limits: that there may be other unknown sources of error, is, of course, quite possible; but ought we to conjure up unknown possibilities in order to reduce our results to regularity, in an investigation, the sole purpose of which is to settle whether they are regular or not? Surely, the only rational and scientific method of procedure is to draw the curves in the first place so as to allow not much more error in the points than we know must exist, and then ascertain the results; if such a drawing leads us to obviously incorrect conclusions, or to conclusions which are not concordant in the various cases investigated, then, and then only, shall we be justified in assuming the existence of unknown errors.

That a second differentiation deals with quantities which are, in most cases, within the limits of the error of the experimental points, is quite true (and this is the reason why the second differentiation can hardly ever be performed on the experimental values themselves), but a curve which is drawn to represent a series of points smooths out the errors of each individual point, and diminishes this error in proportion to the number of points available for the drawing, just as the mean of many repeated determinations gives a result which is more accurate than each separate determination.

Near the point at which two curves meet the differences in their readings will, of course, be very small, and at the point of junction, nil: but the existence of the two curves does not depend on the differences between the points at or near their junction, but on the position of the many points (generally 6 or 7) on either side of the junction. The question so often asked—on what differences do these changes depend?—is one to which it is impossible to give a satisfactory answer: a small difference would often obliterate certain particular changes (as with some of those in the heat of dissolution, results, which were obliterated by differentiating the values in two series); a greater amount of smoothing will obliterate others (the ultra-smoothed curve); but, smooth over and mutilate the results as much as we can, we still have left *some* changes, which gain but greater prominence as the minor ones become effaced. Such a conclusion is drawn from a study of the most (seemingly) regular portion of the most regular curve dealt with—the heat of dissolution curve—a similar examination of those representing the other properties would but enforce this conclusion more strongly.

The multiplicity of the changes will,* no doubt, prove a stumbling block to the acceptance of my conclusions in some minds. The objection may be raised on either mathematical or chemical grounds. Every one is aware, of course, that a curvilinear figure may be regarded as being made up of a number of straight lines, of segments of circles, or of parabolas, provided we split it up sufficiently. But this is no argument that some particular figure may not in reality be made up of independent parabolas. We can, as a matter of fact, string a series of true parabolic curves together so as to make a continuous and apparently regular figure, but no one could say that such a figure was not made up of parabolas, because any curvilinear figure can be regarded, for certain purposes, and within certain limits, as being made up of such. The question must be settled by inspecting the curves, and deciding whether the number of parabolas into which they split up according to my interpretation at all approaches that theoretically infinite number into which any curvilinear figure, whatever its real nature might be, would split up; whether it is at all possible that a mere mechanical and chance distintegration of curvilinear figures of such very different magnitude and such totally different forms as those representing the densities, dilatation, heat of dissolution, and heat capacity, could result in the production of the same number of parabolas in every case, and all locating the changes at the same points. The impossibility of such a chance result will be apparent, I think, to anyone who gives the matter a fair consideration.

The chemical grounds on which the objection may be raised are still weaker. What reason have we for asserting the improbability of sulphuric acid forming seventeen different hydrates in solution? At present we know nothing whatever of the nature or number of hydrates which may exist in the liquid condition, but we do know that there are cases in which some four or five solid hydrates of the same salt have been isolated† (and that within comparatively narrow limits of composition), and, if so many compounds can exist in the solid form, where they are in a definite and stable condition, the probability is, I think, in favour of the existence of a still larger number in solution, where they are, no doubt, in a partially dissociated condition.

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* And has done so. Arrhenius, *Phil. Mag.*, **28**, 37.

† With sodium carbonate we have eight; with basic ferric sulphate there is evidence of as many as fourteen (*Trans.*, 1883, 182). The isolation of different hydrates has nearly always been the result of chance experiments; a systematic attempt to obtain fresh ones would, no doubt, enlarge the number known very considerably.

It is necessary to draw special attention to the definite and specific evidence of change in a reaction, or property, deducible from changes of curvature such as the present work reveals, as opposed to the loose and insufficient evidence which, it is sometimes argued, is shown by an alteration in the general inclination of a figure. If we start with a curvilinear figure, and prove that on differentiation it ultimately yields, say, two different lines which are straight within the limits of experimental error, we prove that, within these same limits, it consists of two different parabolas—two regular and definite figures, which, we may legitimately conclude, represent two regular conditions or actions of the solutions. But a mere change in the general direction of the figure, such as occur at points of maximum or minimum elevation, can prove no specific changes at all, for it is perfectly obvious that such maxima and minima may occur in the middle of the most regular portions of the whole figure. The position of these specific changes is unaltered by the manner in which the results are expressed, and also by the conditions (such as temperature) under which the determinations are made,[*] and this permanency is one of the strongest arguments in favour of their reality; whereas, with mere general changes of direction, we find the reverse to be the case; the position of a maximum alters according to the mode of expression adopted—as with the densities, the contraction, the first differential, and second differential of the densities,[†] and we may almost add, the expansion by heat, where the maxima occur at 97·5, 68, 73, 49, and 86 (also 33) per cent. respectively—and its position varies also with the temperature, as it must in the case of the densities,[‡] and has been proved (Mendeléeff, *Ber.*, 1886, 387) to do in the case of the contractions.

Agreement of the Results obtained from Different Sources.

The establishment of the particular changes of curvature which I consider exist must depend mainly on the concordance of the results obtained from the different properties studied. These are collected in Table F (next page); the changes which are doubtful are enclosed in circular brackets, and are allowed but half value in deducing the mean; the specially doubtful ones are enclosed in square brackets, and are not included at all in the mean, nor in the following discussion. N.D. signifies that there were insufficient data to show whether a particular change existed or not.

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[*] Unless, of course, we alter the temperature so much that a hydrate is entirely destroyed, or a fresh one makes its appearance.

[†] The maximum in the case of the rectilineal second differential *must* correspond to a specific change; from the examples at our disposal, I should imagine that it also does so in the case of the first differential. Its doing so with the sulphuric acid densities, explains how Mendeléeff, by the inordinate smoothing of this curved figure, was led accidentally to name some of the hydrates which actually do exist.

[‡] My results show that the variation is inappreciable from 8° to 38°, but if the temperature were to be raised sufficiently high to destroy all compounds in solution, the maximum would be altered to 100 per cent.: consequently, its position must be variable.

Of the 17 changes shown, there is one (that at 0·1 per cent.) which could have been indicated by the heat of dissolution results only; of the remaining 16, we have—

1	shown in	two	cases.
1	„	three	„
4	„	four	„
1	„	five	„
7	„	six	„
2	„	seven	„

each "case" meaning either the study of a different property, or of the same property at a different temperature.*

There is not a single instance, I think, where the absence of evidence for any change may not fairly be attributed to the lack of sufficient data, and there can be but little doubt but that all the eight sets of results would have shown all the changes, had they been investigated sufficiently.

The average divergence of the individual results from the mean, as deduced from the 82 cases available, is only 0·388 per cent., there being but nine cases in which it reaches or exceeds 1 per cent.

When we consider the extreme difficulty in determining the exact point at which a change occurs within 1 or even 2 per cent., even where the change itself is undoubted, we must admit that this degree of concordance is quite as good as could possibly have been expected: that it could be accidental is out of the question, and we must remember that, not only were the properties investigated different, but that the greater part, and sometimes all of the solutions used in investigating one property were distinct from those used in the others, the only exceptions to this being the densities of sulphuric acid at 8°, 28°, and 38°.

There can therefore be but little doubt that, though there may be several points where uncertainty still prevails, and where future work

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* I have counted the expansion results as but one case: they should, perhaps, be counted as two, since the four series of density determination yield two independent series of expansion values.

The density results at 18° are further confirmed by their treatment in the form of contractions (p.83).

TABLE F.—*Position (in Percentage Values) of the Changes of Curvature shown by the various Properties of Solutions of Sulphuric Acid examined.*

Densities.				Expansion by heat.	Electric conductivity.	Heat capacity.	Heat of dissolution.	Mean	Molecular composition shown.	Composition of definite hydrates.
At 38°·203	At 28°·064.	At 17°·925.	At 7°·978.							
N.D.	N.D.	N.D.	N.D.	N.D. (*a*)	(99·5)	N.D.	99·35	99·47†	35·4 H_2SO_4, H_2O	36 H_2SO_4 H_2O = 99·493
										(35 ,, ,, = 99·478)
,,	,,	97·2	97·7	97·31	(96·8)	,,	97·3	97·38	6·82 ,, ,,	6 ,, ,, = 97·444
										(7 ,, ,, = 97·030)
93·5	94·0	93·6	94·0	93·84	94·0	,,	93·83	93·89	2·82 ,, ,,	3 ,, ,, = 94·233*
			(88·0)	88·65	—	,,	88·95	88·70	1·44 ,, ,,	3 ,, 2 ,, = 89·095*
84·4	84·5	84·5	84·5	83·37	84·0	,,	84·0	84·24	H_2SO_4, 1·02 H_2O	1 ,, 1 ,, = 84·488*
78·2	77·5	78·0	79·0	78·57	—	,,	79·0	78·43	,, 1·49 ,,	2 ,, 3 ,, = 78·407*
72·8	73·3	72·8	73·3	72·74	[73]‡	,,	73·0	73·04	,, 2·01 ,,	1 ,, 2 ,, = 73·142*
				(61·88)§	[63]‡	,,	—	(61·88)§	—	
59·0	57·0	58·0	(58·0)	56·69	—	,,	59·15	58·14	,, 3·92 ,,	(1 ,, 4 ,, = 57·656*
49·0	50·0	51·0	51·0	49·05	—	,,	49·25	49·92	,, 5·46 ,,	1 ,, 5·5,, = 49·756*
										·1 ,, 5 ,, = 52·137)
			(40·0)	39·15	(37·5)	,,	37·75	38·58	,, 8·70 ,,	1 ,, 9 ,, = 37·701
32·0	29·0	29·5	30·0	28·81	N.D.	,,	28·25	29·59	,, 12·94 ,,	1 ,, 13 ,, = 29·526
N.D.	N.D.	18·5	18·5	19·49	,,	,,	19·15	18·92	,, 23·44 ,,	1 ,, 24 ,, = 18·492
,,	,,	8·8	10·5	10·49	9·5	9·85	9·0	9·69	,, 50·8 ,,	1 ,, 58 ,, = 8·585‖
										(1 ,, 50 ,, = 9·821)
,,	,,	4·0	4·3	4·00	3·5	4·1	4·07	3·99	,, 131 ,,	1 ,, 130 ,, = 4·021
,,	,,	1·05	1·05	—	N.D.	1·0	1·13	1·06	,, 508 ,,	1 ,, 510 ,, = 1·057
										(1 ,, 500 ,, = 1·080)
,,	,,	0·25	0·35	(0·35)	,,	N.D.	0·40	0·34	,, 1600 ,,	1 ,, 1500 ,, = 0·362
										(1 ,, 1600 ,, = 0·339)
,,	,,	N.D.	N.D.	N.D.	,,	,,	0·105	0·105	,, 5182 ,,	1 ,, 5000 ,, = 0·109
										1 ,, 5200 ,, = 0·104

(*a*) The values in this column are 7/10000ths lower than those in Table E (p. 118), where the later determinations of the strength of the acid were taken.

† The values for the means are 7/10000ths higher than they should be according to the numbers in the first eight columns, the alteration having been made in accordance with the later determinations of the strength of the acid.

‡ 73 or 63 per cent., but very uncertain.

§ This change is too doubtful to be counted.

‖ The position of this change is defined so much more clearly by the experimental curve of the heat of dissolution (8·7 per cent.) than by any other curve that I have taken the composition indicated by this to be the more probable one.

may introduce some modifications, the great majority of the changes which I have mentioned as existing are established beyond all reasonable question.

Composition of the Hydrates Indicated.

Strong presumptive evidence in favour of the changes here indicated will be afforded if it be found that they occur at percentages corresponding to simple molecular proportions.

Unfortunately, however, there are but seven cases from which any conclusion on this head may be drawn, cases, that is, in which the addition of another molecule of water would alter the composition by from 11 to 2 per cent. (marked by an asterisk in the table, p. 127).* From these it is seen that the average difference between the mean position found and that calculated for an exact number of water molecules or half molecules (the latter in three cases) is only 0·226 per cent., or about 0·057 H_2O on the average, the greatest percentage difference (in the case of $H_2SO_4 4H_2O$) amounting to only 0·48, or 1/11th H_2O.† Such differences are well within the limits of the experimental error.‡

That this concordance of position of the changes in curvature with the composition of definite hydrates has not been in any way influenced by a knowledge on my part of the latter, I may confidently affirm, for, throughout nearly the whole of the work, I purposely avoided ascertaining the percentage composition of any hydrates, the only exception to this being the case of the monohydrate, and in spite of my knowledge of its composition, and the probability of its causing some marked change, I noticed no change at all corresponding to it either in the case of the experimental curves for the heat of dissolution or expansion.

The changes in the highest portion of the curves are of interest, inasmuch as their discovery was the outcome of theoretical considerations, as well as of a reliance on the correctness of the results obtained in the other portions of the curve. The former were, that, just as a weak solution of acid in water contains compounds of the acid molecule with many water molecules, so should a weak solution of water in acid contain compounds of a water molecule with many acid molecules, for in all very weak solutions the solvent acts as a polymer of its fundamental molecule, comparable, if not identical, with the polymers which constitute a mass of the pure liquid* (Trans., 1888, 872, and 1889, 23). The practical considerations were, that, if the second differential were really rectilineal, as the bulk of the figure showed it to be, an apparent curvature in any part of it could only be due to the lack of sufficient points to resolve it into straight lines; this had been proved to be the case with the curved portion of the second differential near the zero end, and, it was argued, it would probably be the case also with the curved portion at the 100 per cent. end.

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* The last column contains a few percentages which do not refer to the hydrates indicated by the determinations; they will be of use in showing the alteration in percentage with molecular composition.

† The greatest difference in molecular composition is with $3H_2SO_4 H_2O$, where it amounts to one-sixth H_2SO_4, but only 0·3 per cent.

‡ The addition of the results arrived at in the case of the calcium salts would double the force of this conclusion.

Looking at the constitution of the various hydrates, there are some signs, in the extreme cases, of the higher ones bearing a simple relation to the lower ones: thus, the water molecules contained in the three highest hydrates are about 500, 1,500, and 5,000, whilst the four compounds richest in acid contain about 36, 6, 3, and 3/2 H_2SO_4 to every H_2O. But such indications must be accepted with great reservation, owing to the impossibility of determining the exact molecular composition in the cases in point. Between the less complex hydrates there would seem to be no simple numerical relation at all.

The great complexity of the hydrates in very weak solutions is one of the most remarkable facts brought to light by the present work, and is such that many chemists will, no doubt, find difficulty in accepting it.† That there should be such things as chemical compounds containing several hundred, and even several thousands of molecules of one of their constituents, all bound together and united (however loosely) with 1 mol. of the other constituent, is indeed a most remarkable fact, and one which must necessitate no unimportant extension of our views as to chemical action. Yet these changes are amongst the best established in the whole work, and they are, moreover, precisely similar in character to those changes in the region of stronger solutions, which certainly do coincide with definite hydrates. If the liquid and gaseous conditions be really continuous, it follows, I think, that the *average composition* of the aggregates composing a mass of water must be about 1800 H_2O, and, if these aggregates combine as such with any dissolved substance (as, from the heat of neutralisation, I argue they must), the hydrates formed will have a corresponding complexity of composition. We should not therefore be surprised at a hydrate containing even 5000 H_2O.

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* The highest compounds recognised would be less complicated in the case of very strong than in that of very weak solutions; a body consisting of 5000 $H_2SO_4H_2O$ would contain only 0·004 per cent. of water, and its recognition here would have been practically impossible.

† Our opinions are naturally biassed by the fact that our experience is inevitably confined, in the majority of cases, to stable compounds. Their stability is but a consequence of the simplicity of their structure; we are here dealing with unstable compounds.

The existence of such compounds gives, I think, an explanation of how "traces" of foreign matter may influence the properties of a body in a manner altogether disproportionate to the amount present, and how the effect produced may be modified or reversed by altering the proportions of the foreign substance, as, for instance, in the case of bismuth in gold, antimony in copper, silicon and carbon in iron, &c.

The comparative magnitude and frequency of the changes at the extreme ends of the curves is but a consequence of the method used for depicting the results. Percentage composition has no scientific meaning, and is but a convenient mode of expressing results: matter must be regarded as consisting of molecules, and the real nature of a mixture or compound is indicated by the relative number of the different molecules present: a small difference of, say, 0·7 per cent., such as that from 1 to 0·3 per cent., really means a trebling of the relative proportions of water and acid present, and the curve representing any action between the two points should extend over three times the distance of the whole of the rest of the diagram from 1 per cent. upwards.

In Fig. 16 I have given a sketch of one set of my results (the second differential of the densities of sulphuric acid at 8°) plotted out against molecular composition. The relative number of molecules are given at the top of the plate. The proportions of 1 : 1 would occupy the centre of the diagram, if the investigations had been pushed to the same limits with strong solutions as with weak ones. It has not been practicable to represent any changes beyond the one at 3·9 per cent., and many of them are seen with such difficulty that their position has had to be specially marked.* The relative magnitude of the changes at the simpler and more complex hydrates, as well as the relative magnitude of the different hydrates amongst the simpler ones, is very striking. The most conspicuous are those at 30, 50, 84, and 94 per cent. corresponding with hydrates with 13, 5·5, 1, and 1/3 H_2O.

It is very evident that this method of plotting out the results would, in most cases, be very unsuitable for working purposes.

Indication of the Monohydrate in Solution.

That the monohydrate exists in solution is, in my opinion, proved by the fact that we can crystallise it out from solutions. The

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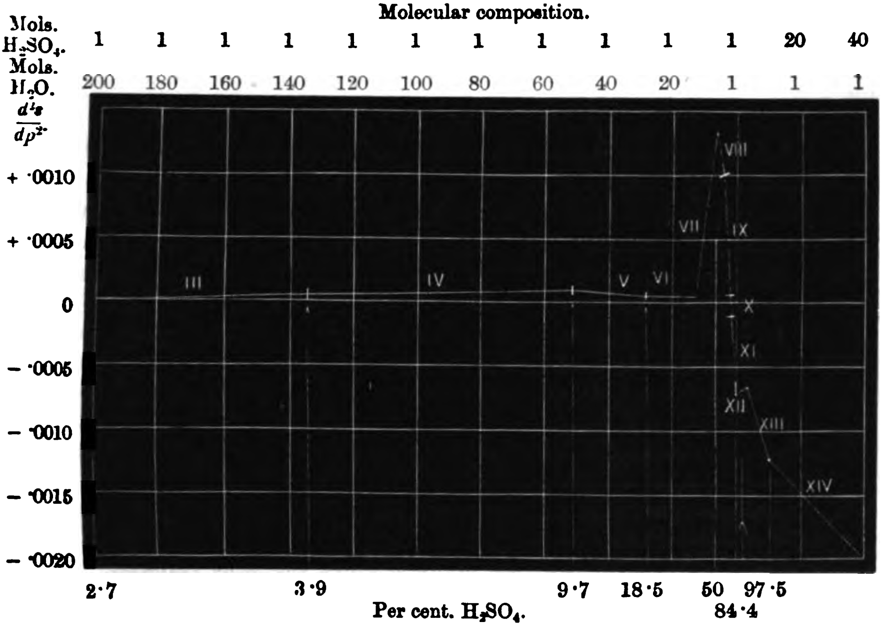
* The constituent lines are numbered so as to correspond with those in Pl. 3.

FIG. 16.—Densities of Sulphuric Acid Solutions.
Second differential plotted against molecular composition.



existence of a body in the crystalline form is not, however, entirely dependent on the stability of its molecules in the liquid condition, but on the ease with which these molecules coalesce to form the aggregates of which it is composed in the solid condition; it does not follow, therefore, that the monohydrate must necessarily be conspicuously stable when liquid, or that the change in curvature indicating its presence should be more marked than those indicating other hydrates in solution. At first sight it appears that such is not the case: the experimental curve for the heat of dissolution shows no discernible change at this point (84·5 per cent.); in the expansion curve it is but feebly marked, and in the first differential of the densities it is by no means prominent. But in all these cases it is found that a repeated application of differentiation (wherever the data are sufficient) alters this, and shows that the change at the monohydrate is really a prominent one (see especially Fig. 2, B, p. 80). Its being partially masked in the experimental curves may, I believe, be due to the fact that this hydrate is really exceptionally stable while liquid, and that, just like the other stable liquids, water and the pure acid, forms compounds containing several fundamental molecules of itself with a single water molecule on the one hand, and a single sulphuric acid molecule on the other; the proximity of the minor changes due to such compounds would, in the absence of a very large number of experimental points, result in the rounding off of the change which shows the monohydrate itself.*

Nature of the Various Curves.

For the chief conclusions drawn from the present work—the existence of more or less sudden changes of curvature at certain points—it is important to show that the various constituent curves differentiate eventually into lines which are straight within the limits of experimental error; for their doing so shows that they are each of them single and simple curves within these same limits. But, apart from these practical considerations, the nature of the constituent curves raises several important questions of theoretical interest: whether the second differential lines are absolutely straight, whether the first differential lines are sometimes so, and whether the constituent curves of the original figure meet tangentially or otherwise. These questions can be answered only with great hesitation.

That a single differentiation is insufficient to reduce the densities (and contractions) and electric conductivities to straight lines, is beyond doubt; with the heat of dissolution, the heat capacity, and the expansion, the case is more doubtful; but the fact that a considerable portion of the first differential figure of all these properties is curved, renders it most probable that it should be curved throughout, and that the straightness observed in parts is but a consequence of comparative magnitude of the error of the determinations and the small scale on which these have to be plotted in consequence.

Whether the straightness of the lines composing the second differentials is merely the result of repeated differentiation, or whether they are straight owing to the nature of the experimental curves from which they are derived (that is, owing to these curves being parabolas of the third order), is a difficult question to settle.

It is true that the majority of (but by no means all) curves of a gentle nature, such as are here dealt with, would yield straight lines on repeated differentiation;† but, for the following reasons, I am inclined to think that the straightness of second differential is really a consequence of the parabolic nature of the experimental curves.

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* Since writing the above, two changes in the vicinity of the monohydrate have been revealed by a study of the freezing points of solutions of the acid.

† As instructive instances of curves which do not do so, I may cite the end portions of the first differential of the densities, and various other gentle curves, each drawn as a single curve, but really made up of two or more independent curves, and which, on repeated differentiation, show their complex nature (instances in the densities and heat of dissolution have been quoted above); and, again, curves representing the molecular heat of dissolution plotted against percentage composition, which are not parabolic at all.

(1.) The curvature of the first differential is often greater than that of the experimental curve, and the straight lines which it yields on further differentiation cannot, therefore, be of a result of a gradual straightening process.*

(2.) The second differential lines are straight in nearly every instance, in spite of the great variations in the curvature of the various first differentials which yield them.

(3.) The first differential of the densities differentiates into straight lines, whereas the experimental curve of the expansions—a curve comparable in its nature and curvature with the density first differential—differentiates, in most parts, into a series of curves.

(4.) Wherever a curved second differential has been obtained, its curvature has been found to be the result of insufficient data.

The question has been raised as to what limit we should put to the process of differentiation (Morley, Proc., 1888, 127), and Crompton's answer—that "a limit to the differentiation would necessarily have to be made according to the nature of the case under investigation, and the discretion exercised by the investigator"—has, I think, been somewhat misunderstood (see Arrhenius, *Phil. Mag.*, **28**, 37). For the purposes of the present work, the limit to be put to the process of differentiation is that at which we get a rectilineal figure, for a straight line is the only form of line which, on mere inspection, is evidently regular, and which must prove regularity in the curve which yields it. A further differentiation would not add to our knowledge (unless we wished to determine diagrammatically the constants in the equations for the curves), for our series of straight lines would simply yield thereby a series of horizontal lines at different levels, and a still further differentiation would yield nothing at all.

A practical limit to the differentiation will also be determined in each individual case by the error of the original experiments. Even when we reduce these errors by taking the curve which represents them, instead of the actual experimental values, there are few cases in which we could proceed beyond a second differentiation so as to obtain results of any value.

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* A comparison of the curvature of the experimental and differential curves is a difficult matter, for the scales used must bear a fixed relationship to each other in the three cases, and the various curves thus produced generally have a different inclination to the axis. Should we determine the curvature in the same *lengths*, or between the same *percentages?* If the former, the curvature of the first differential would nearly always be greater than that of the experimental curve. The expansions and the mixing experiments are the simplest instances to take for such an investigation.

A difference of considerable importance may be noticed between the heat results and the density results. The former are represented throughout by a series of curves, which, on production, cut each other, and from which second differentials will be obtained, which, consequently, do not meet at the points where the change occurs, if indeed they meet at all; whereas the first differentials derived from the densities, and consequently the densities themselves, form a series of curves, which, for the most part, meet tangentially or very nearly so, and the second differentials from these will meet *at* the points of change. This is certainly not always so, but the general tendency is unmistakable. This difference is, no doubt, connected with the difference in the nature of the two properties, the former being a condition of the solutions, the latter a measure of potential energy possessed by them.

The curves for the electric conductivity seem for the most part to be of the same nature as those for the density: the change at 9·5 per cent., however, is a marked exception. The contraction on mixing, the expansion, and the heat capacity, on the other hand, appear to resemble the heat of dissolution more closely; the constituent curves certainly do not meet tangentially, and indeed, in the case of the last, do not appear to meet at all, though, as I have shown above, there must be some connecting link between them (p. 93).

Influence of Temperature on the Hydrates in Solution.

The influence of temperature on the first differential of the densities is of considerable interest. Each figure in Plates 1 and 2* (p. 184) should, if they were all identical, occupy positions five small divisions of the paper below or above its neighbour; but the actual distance between them varies considerably, and shows that all the changes of curvature become more marked as the temperature is lower. The upward curvature at the zero end, and the whole of the constituent curves up to 73 per cent., show this progressive increase very clearly. The portion between 84 and 94 per cent. is also of special interest: it has a decided downwards curvature at 8°, which becomes so slight at 18° and 28°, that it is here practically a straight line, whilst at 38° the curvature is decidedly upwards, and, if we could extend the determinations to still higher temperatures, it would, no doubt, increase, this portion of the diagram becoming less and less distinguishable from the neighbouring curves. The result of this would be that changes in its vicinity would become less marked, and would eventually disappear altogether; the rest of the figure would, no doubt, become simplified in the same way, and would exhibit less and less curvature, till finally reduced to a horizontal line at a temperature sufficiently high to prevent any hydrates at all being formed. The possibility of making determinations would, however, cease long before such a temperature was reached.

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* Including that representing the results collected by Mendeléeff.

But the different hydrates, being of different degrees of stability, will not all disappear at the same temperature, and, consequently, some solutions will show a more or less sudden alteration in the rate at which their density is affected by temperature, under conditions where others, consisting of stabler hydrates, will show no such change. The experimental evidence already discussed tends to confirm this conclusion, and we may reasonably argue that the evidence of sudden changes in the rate of increase of the density with temperature would have been of a more certain character had the method adopted permitted of the examination of very weak solutions, the hydrates in such cases being more complex, and, presumably, less stable, than in the case of strong solutions.

Further evidence as to the existence of such sudden changes has been afforded by my work on the effect of temperature on the heat of dissolution of salts (Trans., 1887, 223), which showed that this property, and, consequently, the heat capacity of the weak solutions obtained in the determinations, exhibited sudden alterations in its rate of increase at certain temperatures.

The highest line in Fig. 15 (p. 120) is also of considerable interest in connection with this point: it represents the rate of increase in the density of water with temperature, and, according to my interpretation of it (details of which cannot be given here), it exhibits abrupt changes at certain points, such as I have concluded would be exhibited by the densities of weak solution, and such as the analogy between the constitution of the weak solutions and of the pure solvent (both being mixtures of molecular aggregates of different degrees of complexity) would lead us to expect.

A consideration of the effects of temperature on the densities must make us recognise the possibility of there being yet other hydrates than those at present discovered, hydrates which would only be revealed by experiments at lower temperatures; it is probable, however, that these would be confined mainly to very weak or very strong solutions. That the densities at 8° should have indicated (though feebly) two changes which were not found at higher temperatures, supports such a conjecture.

Summary and Conclusion.

The curves representing the first differential coefficient of the densities of sulphuric acid solutions form a curvilinear figure, and not a rectilinear figure, as Mendeléeff imagined. This figure, though continuous, is made up of a series of separate curves, which, on further differentiation, yield a series of straight lines.

When we plot out the contractions occurring on mixing sulphuric acid and water, instead of the densities of the solutions obtained, we get a figure totally unlike that formed by the densities: on a first differentiation it gives another curvilinear figure, also totally unlike the first differential of the densities; but, on a second differentiation, a rectilineal figure is obtained, closely resembling the second differential of the densities, and indicating the existence of changes at the same points as the latter does.

The electric conductivities resemble the densities in giving straight lines on a second differentiation only, as shown by Crompton, and they indicate changes at certain points, though the position of these changes are, according to the author, not all identical with those mentioned by Crompton.

The heat capacity is represented by a series of gentle curves, which probably require two differentiations to reduce them to a series of straight lines.

A critical examination of Thomsen's results on the heat evolved by diluting solutions with successive quantities of water leads to the conclusion that the actions are eminently irregular, instead of being regular as he concluded.

The author's present determinations lead to the same results. The heat of dissolution (or dilution) of solutions of different strengths are represented by a series of intersecting curves, each of which requires (in most cases) two differentiations to reduce it to a straight line.

The expansion of sulphuric acid solutions through various ranges of temperature between 8° and 38° gave results which formed irregular curved figures, and these figures split up on two differentiations into a series of straight lines, showing changes at the same points as the other properties did.

An examination of three solutions of sulphuric acid at every 2° showed that the effect of temperature on the densities of these solutions was represented by a single parabola of the second order; but the less numerous density determinations with other solutions indicated that, in some cases, the results cannot be represented by less than two different curves, more or less sudden changes occurring at certain temperatures.

The points at which the changes occur are the same whichever of the above properties be taken for their determination, this concordance placing the existence of the majority of them beyond doubt.

The points at which they occur, moreover, correspond to definite and simple hydrates, considerably within such limits of error as might reasonably be expected.

The hydrates thus recognised amount to as many as 17, the monohydrate being one of them.

The highest hydrates contain a very large amount of water; in the extreme case, as much as $5000H_2O$.

There may be some simple numerical relationship between the constitution of the various hydrates, but only in very weak and in very strong solutions.

As a consequence of the results obtained on analysing the experimental values and the curves representing them, it follows that these latter are represented by a series of parabolas of the third order, such as $s = A + Bp + Cp^2 + Dp^3$, this probably being true in the case of all the properties, though sometimes the last constant is so small in comparison with the experimental error that it may be neglected, and the results be expressed by a parabola of the second order.

In the case of the densities and the electric conductivities, the various curves constituting the first differential appear to meet tangentially, and, consequently, the straight lines constituting the second differential meet *at* the points of change.

This is not the case with the contraction on mixing, the heat of dissolution, or the expansion by heat, the first differential curves (and consequently the experimental curves also), in these cases, intersecting each other on prolongation.

In the case of the heat capacity, the constituent curves representing the experimental values do not appear to meet at all.

The main facts elucidated by this work afford absolute proof that the properties of solutions do not vary regularly with their composition, and that the nature of the solution is, therefore, not merely physical. There can be no doubt but that solutions consist of hydrates of a definite composition, though these may always be in a state of partial dissociation.

It may be urged that, although this may be the case where the solvent is water, in other cases similar compounds would not exist. It is extremely improbable, however, that actions seemingly so analogous as the dissolution of a substance in water and its dissolution in another liquid, should belong to totally different classes of phenomena, the one being chemical, the other physical. It is, however, a question which calls for an answer based on experiment, and, as it would be difficult, if not impossible, to find a solvent other than water with which solutions might be obtained possessing sufficient differences in density, &c., to render them suitable subjects for investigation, some other means of investigation must be adopted. I hope that the freezing points of solutions of different strengths may afford the requisite information, and the results which I have already obtained, since writing the above, from a study of this property in the case of sulphuric acid, justify the expectation that such may be the case.

I am fully aware that the present work supplies material for far more discussion than I have ventured to raise. The precise nature of the changes which occur when solutions are diluted has scarcely been discussed at all. What is the meaning of these various properties being representable by a series of parabolic curves of certain orders? Why should the component curves of the density, the heat of dissolution, and the heat capacity diagrams, show such differences as that of meeting tangentially in one case, cutting each other in the second, and (apparently) not meeting at all in the third case? How can the fact that the changes occur so sharply at the exact composition of certain hydrates be reconciled with the extent to which we must, I think, necessarily imagine that these hydrates are dissociated, even when the water and salt is present in the exact proportions required for their formation (see Trans., 1889, 22)? These, and other questions, I leave for the discussion of abler mathematicians than myself: the present work has no pretentions beyond being an experimental investigation.

But one word remains to be said: a word of thanks to a little girl who has devoted all her spare time to the laborious calculations involved in the present work: to the patience and accuracy of Miss Ethel Willmott all who are interested in the question of the nature of solutions owe much.

TABLE I.—*Densities of Sulphuric Acid Solutions at 17·925°, and First Differentiation.*

p.	s.	$\frac{ds}{dp}$.	p.	Alternate series A and B.			
				$\frac{ds'}{dp'}$.	p'.	$\frac{ds''}{dp''}$.	p''.
Full series, with differences not less than about 1 *per cent.*							
99·85700*	1·834221						
99·85000	1·834281						
99·85350	1·834251 A & B						
		− ·00310	99·34	− ·00310 A	99·34		
		− ·00307	99·32			− ·00307 B	99·32
98·82200	1·837452 A						
98·77812*	1·837550 B						
		− ·00116	98·32	− ·00116 A	98·32		
		− ·00111	98·30			− ·00043 B	97·76
97·82685	1·838610 A						
		+ ·00017	97·29				
96·74952*	1·838428 B			+ ·00057 A	96·92		
		·00116	96·39				
96·02135	1·837587 A					− ·00152 B	95·88
		·00179	95·52	·00224 A	95·06		
95·01355*	1·835781 B						
		·00268	94·51				
93·99780	1·833055 A					·00299 B	94·00
		·00330	93·50	·00378 A	92·81		
92·99056*	1·829734 B						
		·00413	92·31				
91·62209	1·824078 A					·00431 B	92·01
		·00472	91·32	·00504 A	90·83		
91·02467*	1·821258 B						
		·00524	90·53				
90·04606	1·816130 A					·00561 B	90·03
		·00597	89·53	·00628 A	89·00		
89·03102*	1·810075 B						
		·00657	88·49				
87·95802	1·803025 A					·00689 B	88·03
		·00727	87·49	00762 A	86·96		
87·03615*	1·796325 B						
		·00791	86·50				
85·95828	1·787795 A					·00836 B	86·01
		·00884	85·47	·00913 A	84·76		
84·97907*	1·779138 B						
		·00933	84·27				
83·56640	1·765953 A					·00953 B	83·98
		·01000	83·27	·01021 A	82·76		
82·98206*	1·760117 B						
		·01034	82·48				
81·98460	1·749799 A					·01052 B	82·04
		·01071	81·54	·01094 A	80·98		
81·09315*	1·740248 B						
		·01112	80·54				
79·98477	1·727926 A					·01125 B	80·04
		·01140	79·48	·01141 A	79·12		
78·98995*	1·716598 1·716570 } B						
		·01143	78·62				
78·25462	1·708182 A						
		·01167	77·11				
75·95699	1·681361						
		·01175	74·98				
74·00440	1·658412						
		·01177	73·01				
72·02272	1·635093						
		·01171	71·06				
70·09785	1·612557						
		·01159	69·10				
68·10148	1·589410						
		·01147	67·12				
66·13310	1·566839 A						
		·01131	65·51	·01132 A	65·12		
64·89103	1·552790						
		·01133	64·50				
64·11204	1·543960 A						
		·01113	63·08				
62·04053	1·520910						
		·01094	61·01				
59·98903	1·498474 A						
		·01073	58·94	·01060 A	57·94		
57·88930	1·475942						
		·01047	56·89				
55·87689	1·454879 A						
		·01027	54·89				
53·89570	1·434523						
		·01005	52·91				
51·91839	1·414643						
		·00982	50·91				
49·90183	1·394858						
		·00960	48·91				
47·92908	1·375924						
		·00938	46·94				
45·95306	1·357386						
		·00920	44·99				
44·02251	1·339628						

Table I—*continued.*

p.	s.	$\frac{ds}{dp}$.	p.	Alternate series A and B.			
				$\frac{ds'}{dp'}$.	p'.	$\frac{ds''}{dp''}$.	p''.
44·02251	1·339628						
		·00898	43·00				
41·97705	1·321255						
		·00884	40·98				
39·99233	1·303711						
		·00868	39·01				
38·03978	1·286773						
		·00854	37 01				
35·99021	1·269262						
		·00842	35·01				
34·03459	1·252802						
		·00831	33·01				
31·99420	1·235836						
		·00822	31·00				
30·03628	1·219752						
		·00811	29·05				
28·06891	1·203804						
		·00803	27·14				
26·21825	1·188953						
		·00793	25·12				
24·01732	1·171509						
		·00782	23·04				
22·06137	1·156221						
		·00772	21·05				
20·04282	1·140640						
		·00759	19·02				
18·00597	1·125186						
		·00749	17·00				
15·99627	1·110138						
		·00736	15·00				
13·99655	1·095416						
		·00725	13·07				
12·13767	1·081045 C						
		·00710	10·97				
9·804053	1·065349 A						
		·00695	9·387				
8·970256*	1·059554 B						
		·00704	8·463	·00706 C	10·05		
7·955370	1·052408 A & C						
		·00680	7·459	·00700 A	8·85		
6·962185*	1·045656 B						
		·00690	6·494			·00692 B	7·966
6 025176	1·039192 A						
		00675	5·471	·00685 A	6·99		
4·915919*	1·031704 B						
		·00672	4·460			·00682 B	5·939
4 003331	1·025572 A						
		·00669	3·523	·00674 A	5 01		
3·042904	1·019150						
		·00665	2·420				
1·796562	1·010864						
		·06665	1·397				
0·997007	1·005548						
		·00687	0·499				
0	0·998695						
Strong solutions.							
99·85350	1·834251 A						
		— ·00424	99·776				
99·69763*	1·834912 B			— ·00391 A	99·686		
		— ·00363	99·608				
99·51810*	1·835563 A					— ·00338 B	99·505
		— ·00317	99·415				
		— ·00335	99·412			— ·00347 B	99·501
99·31215*	1·836214 B						
				— ·00308 A	99·363		
99·30558*	1·836274 B						
		— ·00293	99·260			— ·00298 B	99·208
		— ·00251	99·256			— ·00273 B	99·199
99·20729*	1·836521 A						
		— ·00292	99·108				
99·09372*	1·836853 B			— ·00272 A	99·096		
		— ·00252	99·039				
98·98452*	1·837128 A					— ·00273 B	98·958
		— ·00199	98·903				
		— ·00204	98·881			— ·00229 B	98·936
98·82200	1·837542 B			— ·00195 A	98·827		
93·77812*	1·837550 B						
		— ·00191	98·745			— ·00173 B	98·670
		— ·00178	98·723			— ·00163 B	98·648
98·66856*	1·837745 A						
		— ·00153	98·594				
98·51877*	1·837974 B			— ·00126 A	98·402		
		— ·00115	98·328				
98·13654*	1·838414 A						
		— ·00063	97·981				
97·82685	1·838610						

TABLE I—*continued.*

Strong solutions—*continued.*

p.	s.	$\frac{ds}{dp}$.	p.	Alternate series A and B.			
				$\frac{ds'}{dp'}$.	p'.	$\frac{ds''}{dp''}$.	p''.
97·82685	1·838610						
		− ·00022	97·677				
97·52668*	1·838693						
		+ ·00012	97·332				
97·13589*	1·838647						
		·00057	96·943				
96·74952*	1·838428						
		·00089	96·559				
		·00100	96·542				
96·36863*	1·838087						
		·00144	96·195				
96·33480	1·838011						
		·00135	96·178				
96·02135*	1·837587						

Weak solutions.

p.	s.	$\frac{ds}{dp}$.	p.	$\frac{ds'}{dp'}$.	p'.	$\frac{ds''}{dp''}$.	p''.
4·915919*	1·031704						
		·00674	4·635				
4·355266*	1·027924						
		·00668	4·179				
4·003331	1·025572						
		·00680	3·905				
3·806007	1·024231						
		·00668	3·610				
3·413022	1·021607						
		·00664	3·228				
3·042904	1·019150						
		·00667	2·819				
2·594819	1·016163						
		·00660	2·409				
2·222768	1·013706						
		·00667	2·010				
1·796562	1·010864						
		·00662	1·602				
1·407762	1·008291						
		·00668	1·202				
0·997077	1·005548						
		·00661	0·902				
0·807416	1·004294						
		·00674	0·703				
0·599067	1·002889						
		·00683	0·499				
0·399816	1·001528						
		·00692	0·301				
0·202068	1·000159						
		·00706	0·152				
0·101357	0·999448						
		·00743	0·056				
0	0·998695						

p.	s.	$\frac{ds}{dp}$.	p.	$\frac{ds'}{dp'}$.	p'.	$\frac{ds''}{dp''}$.	p''.
0·296800*	1·000831						
		·00688	0·222				
0·147963*	0·999807						
		·00714	0·099				
0·049453*	0·999104						
		·00827	0·025				
0	0·998695						

TABLE II.—*Densities of Sulphuric Acid Solutions at 7·978°, 28·064°, and 38·205°, and First Differentiation.*

p.	7·978°		28·064°		38·205°		p.
	s.	ds/dp.	s.	ds/dp.	s.	ds/dp.	
99·85700	1·844560		1·824246		1·814298		
		− ·00299		− ·00301		− ·00327	99·32
98·77812	1·847784		1·827492		1·817828		
						− ·00096	98·28
		− ·00089		− ·00092		− ·00081	98·15
97·78818					1·818780		
97·52668	1·848901		1·828646		1·818836		
						+ ·00026	97·27
		+ ·00033		+ ·00043		·00042	97·14
96·74952	1·848646		1·828308		1·818515		
		·00113		·00116		·00127	96·31
95·87631	1·847660		1·827296		1·817403		
		·00185		·00198		·00204	95·45
95·01355	1·846066		1·825592		1·815640		
		·00249		·00273		·00283	94·46
93·90505	1·843306		1·822561		1·812510		
		·00342		·00348		·00360	93·45
92·99056	1·840179		1·819375		1·809215		
		·00394		·00417		·00428	92·43
91·86622	1·835750		1·814691		1·804407		
		·00458		·00480		·00492	91·45
91·02467	1·831899		1·810652		1·800268		
		·00523		·00546		·00555	90·44
89·85667	1·825796		1·804277		1·793788		
		·00580		·00608		·00616	89·44
89·03102	1·821006		1·799251		1·788694		
		·00652		·00664		·00678	88·44
87·83725	1·813232		1·791296		1·780606		
		·00729		·00752		·00754	87·44
87·03615	1·807388		1·785271		1·774564		
		·00788		·00788		·00790	86·45
85·85956	1·798115		1·776002		1·765265		
		·00889		·00880		·00873	85·42
84·97907	1·790292		1·768252		1·757576		
		·00932		·00918		·00914	84·56
84·01970	1·781343		1·759444		1·748805		
		·00995		·00983		·00963	83·51
82·98206	1·771021		1·749241		1·738808		
		·01056		·01011		·01007	82·42
81·85008	1·759072		1·737792		1·727413		
		·01110		·01066		·01033	81·47
81·09315	1·750673		1·729727		1·719593		
		·01122		·01093		·01087	80·53
79·96809	1·738076		1·717424		1·707359		
		·01164		·01129		·01111	79·48
78·98995	1·726694		1·706389		1·696495		
		·01163		·01131		·01117	78·47
77·94749	1·714570		1·694596		1·684849		
		·01176		·01152		·01139	76·92
75·90717	1·690580		1·671094		1·661610		
		·01187		·01165		·01157	74·95
73·98643	1·667782		1·648712		1·639397		
		·01183		·01164		·01154	73·01
72·02232	1·644541		1·625844		1·616740		
		·01181		·01166		·01157	70·98
69·93139	1·619860		1·601468		1·592543		
		·01168		·01152		·01144	68·97
68·00851	1·597410		1·579326		1·570547		
		·01151		·01139		·01132	67·02
66·02517	1·574588		1·556737		1·548091		
		·01140		·01124		·01118	65·03
64·04535	1·552015		1·534480		1·525956		
		·01125		·01115		·01096	62·98
61·91205	1·528012		1·510701		1·502586		
		·01092		·01074		·01076	60·95
59·97052	1·506801		1·489842		1·481687		
		·01092		·01074		·01070	58·91
57·85589	1·483720		1·467133		1·459055		
		·01051		·01042		·01037	56·93
56·00914	1·464315		1·447899		1·439903		
		·01035		·01022		·01016	55·00
54·00142	1·443536		1·427382		1·419514		
		·01007		·00997		·00993	52·71
52·02681	1·423653		1·407699		1·399899		
		·00990		·00978		·00975	51·05
50·06998	1·404296		1·388553		1·380826		
		·00965		·00957		·00951	49·05
48·02648	1·384578		1·369025		1·361383		
		·00943		·00935		·00931	46·65
45·71655	1·362804		1·347438		1·339889		
		·00917		·00911		·00908	44·65
43·58981	1·343309		1·328068		1·320568		
		·00901		·00894		·00892	42·58
41·76736	1·326892		1·311779		1·304308		
		·00883		·00878		·00874	40·71
39·64778	1·308168		1·293169		1·285783		
		·00868		·00862		·00859	38·69
37·73112	1·291527		1·276647		1·269316		
		·00855		·00848		·00844	36·72
35·71882	1·274323		1·259589		1·252326		
		·00847		·00837		·00832	34·78
33·85203	1·258517		1·243964		1·236792		
		·00834		·00824		·00817	32·83
31·80782	1·241463		1·227117		1·220101		

Table II—*continued.*

p.	7·978°.		28·064°.		38·205°.		*p.*
	s.	*ds/dp.*	*s.*	*ds/dp.*	*s.*	*ds/dp.*	
31·80782	1·241463	·00827	1·227117	·00811	1·220101	·00811	30·79
29·78239	1·224724	·00818	1·210687	·00803	1·203677	·00794	28·77
27·75282	1·208121	·00812	1·194382	·00790	1·187565	·00783	26·96
26·16642	1·195236	·00804	1·181842	·00781	1·175151	·00772	25·00
23·83699	1·176502	·00795	1·163649	·00768	1·157168	·00758	22·87
21·92292	1·161292	·00787	1·148945	·00760	1·142654	·00750	20·88
19·84133	1·144905	·00775	1·133122	·00740	1·127048	—	19·01
18·18353	1·132053		1·112085				

Alternate Determinations.

97·52668	—	—	1·828646	·00082	—	—	96·70
95·87631	—		1·827296		—		
95·01355	1·846066	·00291	1·825592	—	—	—	94·00
92·99056	1·840179		1·819375		—		
89·03102	—	—	1·799251	·00701	1·788694	·00708	88·03
87·03615	1·807388	·00831	1·785271	·00827	1·774564	·00826	86·01
84·97907	1·790292	—	1·768252	·00952	1·757576	—	83·98
82·98206	1·771021	·01077	1·749241	·01033	—	—	82·04
81·09315	1·750673	·01140	1·729727	—	—	—	80·04
78·98995	1·726694		—		—		
81·85008	1·759072	·01116	—		1·727413	·01066	80·91
79·96809	1·738076	·01163	1·717428	·01130	1·707359	·01114	78·96
77·94749	1·714570	—	1·694596		1·684849	·01147	75·97
73·98643	1·667782	·01182	1·648712	·01165	1·639307	·01156	71·96
69·93139	1·619860		1·601468		1·592543		
66·02517	—	—	—	—	1·548091	·01106	63·97
61·91205	1·528012	·01092	—	—	1·502586	·01073	59·88
57·85589	1·483720	·01043	—	—	1·459055	—	56·93
54·00142	1·443536		—		—		
64·04535	—	—	1·534480	·01088	—	—	60·95
57·85589	—		1·467133		—		
33·85203	—	—	—	—	1·236792	·00814	31·82
29·78239	—		—		1·203677		

TABLE II—*continued.*

Other Determinations at 7·978°.

1 per cent. series.

p.	*s.*	*ds/dp.*	*p.*
18·18353	1·132053		
		·00767	16·96
15·73349	1·113271		
		·00755	14·83
13·92476	1·099626		
		·00747	12·91
11·90393	1·084542		
		·00734	10·96
10·01181	1·070660		
		·00725	9·49
8·97026	1·063110		
		·00719	8·46
7·94729	1·055752		
		·00716	7·45
6·96219	1·048704		
		·00711	6·93
		·00706	6·44
5·92138	1·041353		
		·00702	5·42
4·91592	1·034300		
		·00698	4·34
3·76125	1 026234		
		·00692	3·37
2·97588	1·020800		
		·00691	2·38
1·77511	1·012505		
		·00695	1·39
0·99888	1·007108		
		·00723	0·50
0	0·999890		

Strong solutions, full series.

p.	*s.*	*ds/dp.* Alternate dets.	*p.*
99·85700	1·844560 A		
99·69763	1·845196 B	– ·00386 A	99·687
99·51810	1·845867 A	– ·00343 B	99·497
99·30558	1·846542 B	– ·00300 A	99·363
99·20729	1·846800 A	– ·00271 B	99·202
99·09372	1·847115 B	– ·00251 A	92·097
98·98453	1·847359 A	– ·00212 B	98·941
98·77812	1·847784 B	– ·00186 A	98·827
98·66856	1·847948 A	– ·00151 B	98·648
98·51877	1·848176 B	– ·00132 A	98·402
98·13654	1·848651 A		

Strong solutions—(*continued*).

p.	*s.*	*ds/dp.*	*p.*
98·13654	1·848651		
		– ·00063	97·69
97·78818	1·848861		
		– ·00016	97·66
97·52668	1·848901	– ·00001	97·46
		+ ·00009	97·33
97·13689	1·848865		
		·00057	96·94
96·74952	1·848646		
		·00094	96·54
96·33480	1·848257		
		·00131	96·10
95·87631	1 847660		

Weak solutions, full series.

p.	*s.*	*ds/dp.*	*p.*
4·91592	1·034300		
		·00704	4·685
4·35527	1·030357	·00698	4·338
		·00694	4·058
3·76125	1·026234		
		·00690	3·548
3·33425	1·023286		
		·00694	3·154
2·97588	1·020800		
		·00692	2·780
2·58432	1·018089		
		·00691	2·394
2·20353	1·015459		
		·00690	1·989
1·77511	1·012505		
		·00696	1·577
1·37881	1·009748		
		·00695	1·188
0·99888	1·007108		
		·00696	0·896

p.	*s.*	Alternate dets.	*p.*
0·79381	1·005680 A		
0·59736	1·004289 B	·C0708 A	0·593
0·39182	1·002831 A	·00708 B	0·447
0·29680	1·002160 B	·00723 A	0·295
0·19901	1·001435 A	·00743 B	0·222
0·14796	1·001055 B	·00761 A	0·149
0·09852	1·000670 A	·00764 B	0·099
0·04945	1·000302 B	·00792 A	0·049
0	0·999890 A		

TABLE III.—*Densities of Sulphuric Acid Solutions at* 38·203°, 28·064°, 17·925°, *and* 7·978°.

Second Differentiation from the Smoothed First Differential Curves.

p.	At 38·203°.		At 28·064°.		At 17·925°.		At 7·978°.		p.
	$\frac{ds}{dp}10^6$.	$\frac{d^2s}{dp^2}10^6$.	$\frac{ds}{dp}10^6$.	$\frac{d^2s}{dp^2}10^6$.	$\frac{ds}{dp}10^6$.	$\frac{d^2s}{dp^2}10^6$.	$\frac{ds}{dp}10^6$.	$\frac{d^2s}{dp^2}10^6$.	
1 per cent. series.									
99	−2450	−1820	−2320	−1650	−2420	−1690	−2280	−1560	98·5
98	−630	−1210	−670	−1210	−780	−1210	−720	−1150	97·5
97	+580	−1000	+540	−980	+480	−1000	+430	−970	96·5
96	1580	−830	1520	−810	1480	−810	1400	−790	95·5
95	2410	−730	2330	−740	2290	−710	2190	−730	94·5
94	3140	−760	3070	−690	3000	−670	2920	−650	93·5
93	3900	−670	3760	−660	3670	−630	3570	−660	92·5
92	4570	−660	4420	−660	4300	−660	4230	−640	91·5
91	5230	−630	5080	−650	4960	−660	4870	−660	90·5
90	5860	−630	5730	−670	5620	−660	5530	−650	89·5
89	6490	−600	6400	−630	6280	−640	6180	−660	88·5
88	7090	−600	7030	−650	6920	−660	6840	−710	87·5
87	7690	−570	7670	−630	7580	−680	7550	−710	86·5
86	8260	−560	8300	−630	8260	−670	8260	−700	85·5
85	8820	−460	8930	−560	8930	−620	8960	−690	84·5
84	9380	−490	9490	−480	9550	−550	9650	−580	83·5
83	9870	−420	9970	−430	10100	−470	10230	−490	82·5
82	10290	−340	10400	−370	10570	−370	10720	−390	81·5
81	10630	−270	10770	−290	10940	−290	11110	−310	80·5
80	10900	−220	11060	−220	11230	−210	11420	−200	79·5
79	11120	−140	11280	−140	11440	−140	11620	−80	78·5
78	11260	−110	11420	−120	11580	−60	11700	−70	77·5
77	11370	−90	11540	−70	11640	−80	11770	−30	76·5
76	11460	−70	11610	−50	11720	−50	11800	−40	75·5
75	11530	−40	11660	−30	11770	−10	11840	−10	74·5
74	11570	−3	11690	—	11780	−10	11850	0	73·5
73	11600	+10	11690	+4	11770	+2	11850	+20	72·5
72	11570	42	11647	42	11750	53	11818	43	71·0
70	11487	55	11564	65	11645	61	11727	55	69·0
68	11378	66	11455	67	11623	72	11618	68	67·0
66	11247	80	11322	80	11380	80	11483	79	65·0
64	11088	95	11162	92	11220	94	11325	92	63·0
62	10898	104	10980	102	11033	102	11142	105	61·0
60	10691		10776		10830	105	10933	148	59·5
59	—	108*	—	124*	10703	102	10785	102	58·5
58	10475	102	10528	102	10602	105	10683	106	57·5
57	10373	103	10426	103	10497	102	10577	104	56·5
56	10270	108	10323	105	10395	110	10473	113	55·5
55	10162	104	10218	111	10285	108	10360	115	54·5
54	10058	106	10107	109	10177	112	10245	122	53·5
53	9952	112	9980	113	10065	110	10123	128	52·5
52	9840	115	9885	115	9955		9995	132	51·5
51	9725	96	9770	115	—	116†	9863	108	50·5
50	9629	106	9655	100	9724	111	9755	121	49·0
48	9418	103	9455	100	9503	105	9514	110	47·0
46	9212	95	9255	98	9293	98	9295	98	45·0
44	9023	87	9060	86	9098	88	9100	88	43·0
42	8950	82	8885	81	8923	82	8924	78	41·0
40	8686	77	8724	76	8760	75	8769	68	39·0
38	8032	70	8572	67	8610	63	8630	61	37·0
36	8393	66	8438	67	8484	61	8512	53	35·0
34	8262	60	8305	60	8362	58	8407	44	33·0
32	8142	61	8285	53	8257	46	8320	40	31·0
30	8020	64	8075	53	8165	46	8240	39	29·0
28	7893	60	7970	57	8074	49	8162	40	27·0
26	7774	59	7837	51	7976	51	8082	41	25·0
24	7657	56	7755	54	7874	56	8000	47	23·0
22	7545	55	7648	53	7763	58	7907	50	21·0
20	7435	—	7543	—	7648	56	7808	59	19·5
19	—		—		7592		7749		

* At 59.   † At 51.

TABLE III—*continued.*

p.	At 17·925°.		At 7·978°.		p.
	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	
1 per cent. series.					
19	·007592		·007749		
		·000052		·000039	18·5
18	·007540		·007710		
		·000056		·000040	17·5
17	·007484		·007670		
		·000057		·000047	16·5
16	·007427		·007623		
		·000055		·000047	15·5
15	·007372		·007576		
		·000062		·000052	14·5
14	·007310		·007524		
		·000057		·000057	13·5
13	·007253		·007467		
		·000061		·000059	12·5
12	·007192		·007408		
		·000066		·000060	11·5
11	·007126		·007348		
		·000064		·000066	10·5
10	·007062		·007282		
		·000072		·000062	9·5
9	·006990		·007220		
		·000067		·000063	8·5
8	·006923		·007157		
		·000060		·000059	7·5
7	·006863		·007100		
		·000056		·000050	6·5
6	·006807		·007050		
		·000052		·000050	5·5
5	·006755		·007000		
		·000048		·000047	4·5
4	·006707		·006953		
		·000042		+ ·000043	3·5
3	·006665		·006910		
		+ ·000035		− ·000010	2·5
2	·006630		·006920		
		− ·000070		− ·000105	1·5
1	·006700		·007025		
		− 000340		− ·000410	0·75
0·5	·006870		·007230		
Strong solutions.					
99·8	− ·00418		− ·00420		
		− ·00250		− ·00263	99·6
99·4	− ·00318		− ·00315		
		− ·00213		− ·00228	99·2
99·0	− ·00233		− ·00224		
		− ·00188		− ·00195	98·8
98·6	− ·00158		− ·00146		
		− ·00160		− ·00150	98·4
98·2	− ·00094		− ·00086		
		− ·00135		− ·00128	98·0
97·8	− ·00040		− ·00035		
		− ·00115		− ·00108	97·6
97·4	+ ·00006		+ ·00008		
		− ·00110		− ·00103	97·2
97·0	·00050		·00049		
		− ·00108		− ·00093	96·8
96·6	·00093		·00086		
		− ·00098		− ·00093	96·4
96·2	·00132		·00123		
		− ·00090		− ·00090	96·0
95·8	·00168		·00159		
		− ·00085		− ·00080	95·6
95·4	·00202		·00191		
		− ·00075		− ·00075	95·2
95·0	·00232		·00221		
		− ·00073		− ·00073	94·8
94·6	·00261		·00250		
		− ·00068		− ·00070	94·4
94·2	·00288		·00278		
Weak solutions.					
3·8	·006690		—		
		·000067		—	3·65
3·5	·006670		·006915		
		·000050		+ ·000010	3·25
3·0	·006645		·006910		
		·000020		− ·000010	2·75
2·5	·006635		·006915		
		0		− ·000030	2·25
2·0	·006635		·006930		
		− ·000030		− ·000030	1·75
1·5	·006650		·006945		
		− ·000050		− ·000050	1·25
1·0	{ ·006675 ·006560 }		·006970		
		—			
0·9	·006620		·006950		
		− ·000600		+ ·000200	0·95
0·8	·006685		·007020		
		− ·000650		− ·000700	0·85
0·7	·006740		·007070		
		− ·000550		− ·000500	0·75
0·6	·006795		·007095		
		− ·000550		+ ·000250	0·65
0·5	·00840		·007095		
		− ·000450		0	0·55
0·4	·006890		·007075		
		− ·000500		+ ·000200	0·45
0·3	·006930		—		
		− ·000400		—	0·35
0·24	·006915		—		
		+ ·000250		—	0·27
0·20	·006960		—		
		− ·001130		—	0·22
0·16	·007020		—		
		− ·001500		—	0·18
0·12	·007090		—		
		− ·001750		—	0·14
0·08	·007290		—		
		− ·005000		—	0·10
0·04	·007660		—		
		− ·009250		—	0·06

TABLE III—*continued.*

p.	At 17·925°:		At 7·978°.		p.
	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	$\frac{ds}{dp}$.	$\frac{d^2s}{dp^2}$.	
0·4	—	—	·007075		
				− ·001700	0·375
0·35	—	—	·007160		
				− ·001500	0·325
0·30	—	—	·007235		
				− ·001800	0·275
0·25	—	—	·007325		
				− ·002100	0·225
0·20	—	—	·007430		
				− ·002800	0·175
0·15	—	—	·007570		
				− ·003000	0·125
0·10	—	—	·007720		
				− ·003300	0·075
0·05	—	—	·007885		
				− ·004100	0·025
0	—	—	·008090		

TABLE IV.—*First Differential of the Densities of Sulphuric Acid at 0°, according to Mendeléeff, with Values altered for comparison with Pickering's results.*

p.	$\frac{ds}{dp}$.	$\frac{ds}{dp}$ altered.
95·86	·00110	·00090
87·94	·00693	·00684
83·50	·00995	·00992
80·99	·01110	·01093
76·49	·01177	·01198
71·00	·01177	·01208
64·96	·01138	·01155
56·97	·01056	·01079
43·87	·00916	·00911
32·75	·00836	·00844
24·98	·00799	·00815
14·15	·00751	·00770
7·46	·00714	·00737
3·75	·00695	·00716
1·98	·00692	·00709
0·70	·00715	·00770

Table V.—*Contraction in c.c. on the Formation of* 1 *gram of Sulphuric Acid Solutions at* 17·925°.

Volume of 1 gram of water = 1·001307 c.c.
" " " sulphuric acid = 0·545379 c.c.

p.	Sum of volumes.	Volume of mixture.	Contraction C.	$\frac{dC}{dp}$.	p.
99·85350	·546047	·545184	·000863	− ·005482	99·34
98·82200	·550749	·544232	·006518	− ·005478	99·32
98·77812	·550957	·544203	·006754	− ·004904	98·32
97·82685	·555287	·543889	·011398	− ·004882	98·30
96·74952	·560199	·543943	·016256	− ·004509	97·29
96·02135	·563519	·544192	·019327	− ·004215	96·39
95·01355	·568113	·544727	·023386	− ·004028	95·52
93·99780	·572745	·545539	·027206	− ·003761	94·51
92·99056	·577384	·546527	·030856	− ·003624	93·50
91·62209	·583576	·548222	·035354	− ·003287	92·31
91·02467	·586300	·549071	·037229	− ·003139	91·32
90·04606	·590762	·550621	·040140	− ·002975	90·53
89·03102	·595390	·552463	·042926	− ·002745	89·53
87·95802	·600284	·554627	·045657	− ·002545	88·49
87·03615	·604485	·556692	·047793	− ·002317	87·49
85·95828	·609507	·559348	·050159	− ·002195	86·50
84·97907	·613864	·562169	·051695	− ·001569	85·47
83·56640	·620294	·566266	·054028	− ·001652	84·27
82·98206	·622968	·558131	·054837	− ·001385	83·27
81·98460	·627516	·571494	·056022	− ·001188	82·48
81·09315	·631581	·574631	·056950	− ·001041	81·54
79·98477	·636634	·578729	·057905	− ·000862	80·54
78·98995	·641170	·582552	·058618	− ·000717	79·48
78·25462	·644523	·585418	·059105	− ·000662	78·62
75·95699	·654998	·594754	·060344	− ·00539	77·11
74·00440	·663900	·602987	·060914	− ·000287	74·98
72·02272	·672935	·611586	·061349	− ·000220	73·01
70·09785	·681710	·620133	·061577	− ·000118	71·06
68·10148	·690813	·629165	·061648	− ·000036	69·10
66·13310	·699787	·638228	·061559	+ ·000045	67·12
64·89103	·745451	·643999	·061452	·000086	65·51
64·11204	·709000	·647683	·061347	·000135	64·50
62·04053	·718447	·665701	·060946	·000194	63·08
59·98903	·727716	·667345	·060371	·000280	61·01
57·88930	·737373	·677534	·059839	·000253	58·94
55·87689	·746549	·687342	·059207	·000314	56·89
53·89570	·755581	·697096	·058485	·000364	54·89
51·91839	·764597	·706892	·057705	·000394	52·91
49·90183	·773791	·716919	·056872	·000413	50·91
47·92908	·773791	·716919	·056000	·000442	48·91
45·95306	·782784	·726784	·054984	·000514	46·94
44·02251	·791694	·736710	·054107	·000454	44·99
41·97705	·809921	·756856	·053065	·000509	43·00
39·99233	·819070	·767041	·051929	·000572	40·98
38·03978	·827873	·777138	·050735	·000612	39·01
35·99021	·837217	·787859	·049358	·000672	37·01
34·03459	·846134	·798211	·047923	·000734	35·01

TABLE V—*continued.*

p.	Sum of volumes.	Volume of mixture.	Contraction C.	$\frac{dC}{dp}$.	p.
34·03459	·846134	·798211	·047923		
				·000790	33·01
31·99420	·855440	·809129	·046311		
				·000913	31·00
30·03628	·864363	·819839	·044524		
				·000961	29·05
28·06891	·873333	·830700	·042633		
				·001048	27·14
26·21825	·881770	·841076	·040694		
				·001131	25·12
24·01732	·891805	·853600	·038205		
				·001211	23·04
22·06137	·900723	·864886	·035837		
				·001292	21·05
20·04282	·909926	·876696	·033230		
				·001355	19·02
18·00597	·919213	·888742	·030471		
				·001436	17·00
15·99627	·928375	·900789	·027586		
				·001495	15·00
13·99655	·937493	·912896	·024597		
				·001556	13·07
12·13767	·945968	·924263	·021705		
				·001613	10·97
9·80405	·956599	·938659	·017940		
				·001680	8·85
7·955370	·965036	·950202	·014834		
				·001701	6·99
6·025176	·973836	·962285	·011551		
				·001762	5·01
4·003331	·983054	·975065	·007989		
				·001838	3·52
3·042904	·987433	·981209	·006224		
				·001894	2·42
1·796562	·993116	·989253	·003863		
				·001980	1·40
0·997007	·996762	·994482	·002280		
				·002281	0·49
0		1·001307	0		
8·970256	·960409	·943793	·016616		
				·001688	7·97
6·162185	·969564	·965337	·013227		
				·001762	5·94
4·915919	·978894	·969272	·009622		
Strong solutions.					
100·00000		·545379	0		
				− ·005891	99·927
99·85350	·546047	·545184	·000863		
99·69763	·546758	·544986	·001772		
				− ·005593	99·505
				− ·005617	99·510
99·31215	·548517	·544599	·003918		
99·30558	·548545	·544581	·003964		
				− ·005407	99·26
				− ·005301	99·26
99·20729	·548993	·544508	·004485		
				− ·005433	99·11
99·09372	·549511	·544409	·005102		
				− ·005302	99·04
98·98452	·550009	·544328	·005681		
				− ·005150	98·90
				− ·005199	98·88
98·82200	·550749	·544232	·006518		
98·77812	·550957	·544203	·006754		
				− ·005129	98·75
				− ·005029	98·72
98·66856	·551450	·544145	·007305		
				− ·005007	98·59
98·51877	·552132	·544077	·008055		
				− ·004900	98·33
98·13654	·553875	·543947	·009928		
				− ·004747	97·98
97·82685	·555287	·543889	·011398		
				− ·004641	97·68
97·52668	·556655	·543864	·012791		
				− ·004551	97·33
97·13589	·558443	·543878	·014565		
				− ·004363	96·94
96·74953	·560199	·543943	·016256		
				− ·004293	96·56
				− ·004256	96·54
96·36863	·561934	·544043	·017891		
96·33480	·562088	·544067	·018021		
				− ·004147	96·20
				− ·004167	96·18
96·02135	·563519	·544192	·019327		

TABLE V—*continued.*

p.	Sum of volumes.	Volume of mixture.	Contraction C.	$\frac{dC}{dp}$.	p.
Weak solutions.					
4·915919	·978894	·969272	·009622	— ·001787	4·655
4·355266	·981450	·972830	·008620	— ·001793	4·179
4·003331	·983054	·975065	·007989	— ·001875	3·905
3·806007	·983954	·976335	·007619	— ·001853	3·610
3·413022	·985746	·978855	·006891	— ·001802	3·228
3·042904	·987433	·981209	·006224	— ·001870	2·819
2·594819	·989480	·984094	·005386	— ·001863	2·409
2·222768	·991172	·986479	004693	— ·001947	2·010
1·796562	·993116	·989253	·003863	— ·001929	1·602
1·407762	·994889	·991776	·003113	— ·002028	1·202
0·997077	·996762	·994482	·002280	— ·001972	— ·902
0·807416	·997626	·995720	·001906	— ·002160	— ·703
0·599067	·998576	·997120	·001456	— ·002238	— ·499
0·399816	·999484	·998474	·001010	— ·002357	— ·301
0·202068	1·000385	·999841	·000544	— ·002473	— ·152
0·101357	1·000845	1·000550	·000295	— ·002911	— ·056
0		1·001377	0		
0·296800	·999954	·999163	·000791	— ·002352	— ·222
0·147963	1·000634	1·000193	·000441	— ·002445	— ·099
0·049453	1·001097	1·000897	·000200	— ·004048	— ·025
0		1·001307	0		

TABLE VI.—*Contraction on the formation of Sulphuric Acid Solutions at 17·925°.*

Second Differentiation from the Smoothed First Differential Curve.

p.	$\frac{dC}{dp}10^6$.	$\frac{d^2C}{dp^2}10^6$.	p.	$\frac{d^2C}{dp^2}10^6$. for 1 c.c.
100	−5970			
99	−5270	−700	99·5	−1280
98	−4750	−520	98·5	− 960
97	−4380	−370	97·5	− 680
96	−4100	−280	96·5	− 510
95	−3880	−220	95·5	− 400
94	−3710	−170	94·5	− 310
93	−3480	−230	93·5	− 420
92	−3250	−230	92·5	− 420
91	−3050	−200	91·5	− 360
90	−2840	−210	90·5	− 380
89	−2640	−200	89·5	− 360
88	−2450	−190	88·5	− 340
87	−2270	−180	87·5	− 320
86	−2120	−150	86·5	− 270
84	−1680	—	—	—
83·5	−1440	−280	83·75	− 960
83	−1320	−240	83·25	− 420
82·5	−1200	−240	82·75	− 420
82	−1090	−220	82·25	− 390
81·5	− 990	−200	81·75	− 350
81	− 920	−140	81·25	− 240
80·5	− 850	−140	80·75	− 240
80	− 780	−140	80·25	− 240
79	− 680	−100	79·5	− 170
78	− 600	− 80	78·5	− 140
77	− 520	− 80	77·5	− 140
76	− 400	−120	76·5	− 290
75	− 280	−120	75·5	− 200
74	− 160	−120	74·5	− 200
74	− 273			
72	− 173	− 50	73	− 83
70	− 75	− 49	71	− 79
68	+ 8	− 42	69	− 67
66	90	− 41	67	− 65

p.	$\frac{dC}{dp}10^6$.	$\frac{d^2C}{dp^2}10^6$.	p.	$\frac{d^2C}{dp^2}10^6$. for 1 c.c.
66	90			
64	157	− 34	65	− 53
62	223	− 33	63	− 50
60	220	− 2	61	− 3
58	280	− 30	59	− 44
56	335	− 28	57	− 41
54	375	− 20	55	− 29
52	405	− 15	53	− 21
50	430	− 13	51	− 18
48	443	− 7	49	− 10
44	480	—	—	—
42	533	− 27	43	− 36
40	592	− 30	41	− 39
38	645	− 27	39	− 35
36	705	− 30	37	− 38
34	760	− 28	35	− 35
32	824	− 32	33	− 40
30	910	—	—	—
28	1005	− 48	29	− 58
26	1092	− 44	27	− 53
24	1175	− 42	25	− 50
22	1252	− 39	23	− 45
20	1327	− 38	21	− 44
18	1398	− 33	19	− 37
16	1462	− 35	17	− 39
14	1527	− 33	15	− 36
12	1583	− 28	13	− 30
10	1635	− 26	11	− 28
8	1685	− 25	9	− 27
6	1725	− 20	7	− 21
4	1800	− 38	5	− 39
2	1928	− 64	3	− 65
1	2050	−122	1·5	− 124
0	2380	−330	0·5	− 331

TABLE VII.—*Densities of Sulphuric Acid Solutions at Temperatures between 40° and 0°.*

p = per cent. by weight of H_2SO_4.

p.	40°.	38°.	36°.	34°.	32°.	30°.	28°.	26°.	24°.	22°.	20°.	p.
100·0	1·81217	1·81404 9	1·81603	1·81801	1·81998	1·82195	1·82393 2	1·82590	1·82785	1·82982	1·83180	100·0
99·5	1·81393	1·81590 2	1·81787	1·81984	1·82183	1·82384	1·82584 2	1·82784	1·82982	1·83181	1·83381	99·5
99·0	1·81541	1·81737 1	1·81933	1·82131	1·82327	1·82525	1·82725 2	1·82923	1·83121	1·83319	1·83518	99·0
98·5	1·81644	1·81835 0	1·82028	1·82222	1·82417	1·82612	1·82806 4	1·83004	1·83203	1·83403	1·83604	98·5
98·0	1·81699	1·81886 9	1·82077	1·82269	1·82462	1·82657	1·82852 7	1·83050	1·83250	1·83450	1·83650	98·0
97·5	1·81713	1·81903 0	1·82095	1·82288	1·82483	1·82680	1·82878 5	1·83075	1·83270	1·83465	1·83664	97·5
97·0	1·81695	1·81885 3	1·82076	1·82268	1·82462	1·82658	1·82855 7	1·83052	1·83249	1·83448	1·83650	97·0
96	1·81580	1·81769 6	1·81960	1·82153	1·82349	1·82546	1·82744 8	1·82943	1·83141	1·83342	1·83543	96
95	1·81370	1·81564 3	1·81758	1·81951	1·82146	1·82345	1·82546 3	1·82743	1·82939	1·83142	1·83347	95
94	1·81084	1·81280 0	1·81476	1·81672	1·81870	1·82070	1·82271 1	1·82472	1·82672	1·82873	1·83077	94
92	1·80299	1·80496 0	1·80693	1·80891	1·81092	1·81298	1·81406 2	1·81714	1·81920	1·82125	1·82330	92
90	1·79245	1·79445 7	1·79646	1·79847	1·80054	1·80265	1·80479 8	1·80692	1·80904	1·81116	1·81330	90
88	1·77937	1·78143 9	1·78352	1·78562	1·78772	1·78983	1·79196 4	1·79413	1·79630	1·79844	1·80062	88
86	1·76393	1·76600 4	1·76810	1·77018	1·77229	1·77442	1·77659 2	1·77878	1·78097	1·78317	1·78537	86
*84·5	1·75083	1·75282	1·75485	1·75692	1·75901	1·76114	1·76330	1·76547	1·76763	1·76980	1·77199	*84·5
84	1·74624	1·74826 2	1·75029	1·75238	1·75448	1·75658	1·75869 6	1·76083	1·76297	1·76514	1·76732	84
82	1·72657	1·72856 1	1·73056	1·73258	1·73462	1·73668	1·73874 3	1·74079	1·74288	1·74501	1·74715	82
80	1·70537	1·70728 0	1·70923	1·71120	1·71319	1·71519	1·71721 2	1·71923	1·72125	1·72329	1·72535	80
78	1·68314	1·68500 8	1·68691	1·68883	1·69077	1·69273	1·69465 5	1·69658	1·69853	1·70050	1·70250	78
76	1·66042	1·66224 7	1·66409	1·66694	1·66781	1·66971	1·67160 5	1·67348	1·67538	1·67730	1·67924	76
74	1·63732	1·63912 5	1·64095	1·64277	1·64460	1·64645	1·64831 2	1·65012	1·65197	1·65387	1·65579	74
72	1·61423	1·61597 8	1·61774	1·61952	1·62131	1·62312	1·62496 2	1·62680	1·62862	1·63045	1·63230	72
70	1·59121	1·59293 5	1·59470	1·59645	1·59819	1·59995	1·60174 2	1·60355	1·60536	1·60716	1·60897	70
68	1·56835	1·57006 4	1·57177	1·57350	1·57524	1·57698	1·57873 0	1·58050	1·58225	1·58400	1·58579	68
66	1·54579	1·54745 3	1·54911	1·55079	1·55249	1·55422	1·55597 6	1·55772	1·55946	1·56121	1·56297	66
64	1·52354	1·52517 2	1·52681	1·52846	1·53013	1·53181	1·53351 3	1·53522	1·53694	1·53866	1·54040	64

* 84·5, more accurately 84·4878, the composition of the monohydrate.

TABLE VII—*continued.*

p.	40°.	38°.	36°.	34°.	32°.	30°.	28°.	26°.	24°.	22°.	20°.	p.
62	1·50159	1·50318 4	1·50478	1·50638	1·50801	1·50966	1·51133 7	1·51300	1·31471	1·51645	1·51819	62
60	1·47998	1·48152 6	1·48307	1·48465	1·48625	1·48789	1·48958 2	1·49126	1·49296	1·49466	1·49636	60
58	1·45876	1·46029 8	1·46186	1·46343	1·46502	1·46665	1·46826 9	1·46993	1·47163	1·47331	1·47500	58
56	1·43804	1 43956 5	1·44110	1·44264	1·44428	1·44584	1·44744 6	1·44909	1·45074	1·45241	1·45407	56
54	1·41776	1·41926 7	1·42079	1·42233	1·42388	1·42544	1·42704 1	1·42865	1·43029	1·43194	1·43357	54
52	1·39792	1·39942 3	1·40094	1·40245	1·40398	1·40553	1·40710 9	1·40869	1·41027	1·41186	1·41346	52
50	1·37845	1·37996 1	1·38148	1·38299	1·38451	1·38603	1·38758 3	1·38914	1·39072	1·39229	1·39386	50
48	1·35949	1·36096 6	1·36245	1·36396	1·36548	1·36700	1·36850 1	1·37003	1·37157	1·37313	1·37469	48
46	1·34089	1·34234 5	1·34381	1·34529	1·34678	1·34829	1·34980 6	1·35133	1·35286	1·35440	1·35593	46
44	1·32267	1·32412 7	1·32560	1·32708	1·32857	1·33005	1·33153 7	1·33304	1·33454	1·33604	1·33756	44
42	1·30482	1·30626 3	1·30770	1·30916	1·31063	1·31214	1·31362 6	1·31513	1·31663	1·31812	1·31964	42
40	1·28732	1·28873 7	1·29019	1·29165	1·29309	1·29456	1·29603 5	1·29752	1·29901	1·30048	1·30197	40
38	1·27011	1·27152 2	1·27296	1·27440	1·27685	1·27731	1·27876 5	1·28023	1·28170	1·28318	1·28467	38
36	1·25321	1·25462 8	1·25604	1·25746	1·25889	1·26033	1·26178 7	1·26324	1·26468	1·26612	1·26760	36
34	1·23655	1·23795 3	1·23937	1·24078	1 24220	1·24362	1·24504 6	1·24650	1·24794	1·24938	1·25082	34
32	1·22017	1·22155 4	1·22295	1·22436	1·22576	1·22716	1·22854 7	1·22995	1·23137	1·23279	1·23422	32
30	1·20403	1·20539 5	1·20677	1·20815	1·20953	1·21091	1·21230 2	1·21370	1·21508	1·21646	1·21784	30
28	1·18816	1·18948 8	1·19085	1·10221	1·19355	1·19489	1·19623 3	1·19758	1·19894	1·20032	1·20170	28
26	1·17252	1·17384 4	1·17516	1·17648	1·17780	1·17912	1·18042 9	1·18175	1·18306	1·18438	1·18570	26
24	1·15716	1·15843 0	1·15972	1·16100	1·16228	1·16356	1·16484 4	1·16612	1·16738	1·16866	1·16993	24
22	1·14197	1·14323 1	1·14449	1·14573	1·14699	1·14824	1·14945 5	1·15068	1·15191	1·15314	1·15436	22
20	1·12706	1·12824 3	1·12945	1·13065	1·13185	1·13305	1·13425	1·13545	1·13663	1·13780	1·13898	20
18	1·11254	1·11368	1·11482	1·11597	1·11711	1·11825	1·11939	1·12053	1·12167	1·12279	1 12391	18
16	1·09815	1·09923	1·00033	1·10141	1·10250	1·10360	1·10470	1·10579	1·10684	1·10791	1·10899	16
14	1·08405	1·08511	1·08617	1·08723	1·08827	1·08930	1·09031	1·09133	1·09234	1·09334	1·09434	14
12	1·07025	1·07125	1·07225	1·07325	1·07425	1·07524	1·07621	1·07717	1·07811	1·07905	1·07997	12
10	1 05662	1·05760	1·05856	1·05952	1·06047	1·06139	1·06230	1·06319	1·06407	1·06493	1·06579	10
8	1·04339	1·04429	1·04518	1·04608	1·04696	1·04783	1·04867	1·04951	1·05032	1·05112	1·05192	8
6	1·03048	1·03133	1·03218	1·03301	1·03382	1·03462	1·03541	1·03617	1·03690	1·03760	1·03830	6
5	1·02409	1·02492	1·02576	1·02659	1·02738	1·02814	1·02888	1·02959	1·03027	1·03093	1·03159	5

TABLE VII—*continued.*

p.	40°.	38°.	36°.	34°.	32°.	30°.	28°.	26°.	24°.	22°.	20°.	*p.*
4	1·01776	1·01856	1·01938	1·02018	1·02093	1·02165	1·02235	1·02304	1·02369	1·02431	1·02493	4
3·5	1·01455	1·01534	1·01612	1·01689	1·01765	1·01838	1·01909	1·01978	1·02043	1·02104	1·02162	3·5
3	1·01135	1·01213	1·01190	1·01365	1·01438	1·01510	1·01580	1·01648	1·01712	1·01772	1·01830	3
0·5	1·00824	1·00901	1·00977	1·01052	1·01122	1·01192	1·01261	1·01326	1·01387	1·01446	1·01502	0·5
2·0	1·00508	1·00586	1·00661	1·00735	1·00804	1·00872	1·00939	1·01002	1·01063	1·01119	1·01174	2 0
1·5	1·00211	1·00283	1·00353	1·00422	1·00490	1·00553	1·00616	1·00676	1·00735	1·00791	1·00844	1·5
1·0	0·99878	0·99950	1·00024	1·00095	1·00164	1·00228	1·00292	1·00352	1·00411	1·00465	1·00515	1·0
0·5	0·99567	0·99640	0·99712	0·99783	0·99849	0·99911	0·99971	1·00028	1·00083	1·00132	1·00179	1·5
0	0·99240	0·99314 5	0·99386	0·99453	0·99518	0·99579	0·99636 7	0·99691	0·99742	0·99979	0·99831	0

p.	18°.	16°.	15°.	14°.	12°.	10°.	8°.	6°	4°.	2°.	0°.	*p.*
100·0	1·83378 2	1·83585	1·83689	1·83793	1·84003	1·84212	1·84421 5	1·84634	1·84849	1·85066	1·85284	100·0
99·5	1·83580 8	1·83784	1·83886	1·83988	1·84195	1·84404	1·84612 8	1·84825	1·85038	1·85249	1·85461	99·5
99·0	1·83717 6	1·83921	1·84022	1·84123	1·84328	1·84536	1 84745 5	1·84959	1·85172	1·85382	1·85589	99·0
98·5	1·83805 5	1·84007	1·84109	1·84211	1·84418	1·84625	1·84831 1	1·85039	1·85249	1·85460	1·85671	98·5
98·0	1·83851 2	1·84053	1·84154	1·84256	1·84462	1·84671	1·84879 6	1·85088	1·85300	1·85508	1·85714	98·0
97·5	1·83864 9	1·84068	1·84170	1·84272	1·84476	1·84681	1·84889 6	1·85101	1·85310	1 85516	1·85722	97·5
97·0	1·83850 7	1·84053	1·84154	1·84256	1·84460	1·84665	1·84874 4	1·85092	1·85301	1·85509	1·85719	97·0
96	1·83747 4	1·83950	1·84052	1·84153	1·84357	1·84564	1·84771 9	1·84984	1·85195	1·85406	1·85618	96
95	1·83554 3	1·83760	1·83862	1·83963	1·84165	1·84370	1·84582 9	1·84800	1·85016	1·85230	1·85444	95
94	1·83281 3	1·83486	1·83588	1·83690	1·83980	1·84109	1·84820 0	1·84534	1·84750	1·84968	1·85188	94
92	1·82539 8	1·82751	1·82857	1·82964	1·83176	1·83388	1·83602 1	1·83818	1·84034	1·84250	1·84466	92
90	1·81545 9	1·81760	1·81867	1·81973	1·82186	1·82402	1·82621 1	1·82841	1·83061	1·83281	1·83501	90
88	1·80282 7	1·80505	1·80614	1·80724	1·80946	1·81172	1·81387 0	1·81615	1·81841	1·82067	1·82294	88
86	1·78758 1	1·78982	1·79093	1·79194	1·79414	1·79637	1·79862 2	1·80088	1·80315	1·80542	1·80769	86

TABLE VII—*continued.*

p.	18°.	16°.	15°.	14°.	12°.	10°.	8°.	6°.	4°.	2°.	0°.	*p.*
*84·5	1·77419	1·77639	1·77749	1·77859	1·78079	1 78300	1·78520	1·78740	1·78960	1·89180	1·79402	*84·5
84	1·76951 9	1·77171	1·77280	1·77389	1·77608	1·77829	1·78055 4	1·78283	1·78510	1·78737	1·78964	84
82	1·74929 3	1·75143	1·75250	1·75357	1·75573	1·75788	1·76003 8	1·76219	1·76437	1·76657	1·76877	82
80	1·72740 6	1·72949	1·73052	1·73155	1·73362	1·73570	1·73776 6	1·73986	1·74198	1·74410	1·74622	80
78	1·70448 9	1·70645	1·70744	1·70844	1·71044	1·71247	1·71451 1	1·71655	1·71858	1·72062	1·72266	78
76	1·68118 7	1·68318	1·68416	1·68513	1·68707	1·68904	1·69101 4	1·69293	1·69485	1·69677	1·69871	76
74	1·65769 7	1·65962	1·66058	1·66154	1·66348	1·66541	1·66729 7	1·66915	1·67101	1·67285	1·67471	74
72	1·63418 3	1·63606	1·63699	1·63791	1·63978	1·64167	1·64356 7	1·64551	1·64744	1·64938	1·65132	72
70	1·61080 1	1·61265	1·61357	1·61450	1·61636	1·61822	1·62006 0	1·62195	1·62385	1·62574	1·62764	70
68	1·58762 3	1·58947	1 59038	1·59128	1·59309	1·59492	1·59673 8	1·59860	1·60046	1·60234	1·60422	68
66	1·56475 0	1·56654	1·56744	1·56833	1·57011	1·57189	1·57369 0	1·57551	1·57735	1·57921	1·58105	66
64	1·54215 4	1·54391	1·54478	1·54566	1·54741	1·54915	1·55091 7	1·55272	1·55452	1·55633	1 55815	64
62	1·51993 9	1·52167	1·52252	1·52337	1·52507	1·52678	1·52848 1	1·53024	1·53200	1·53376	1·53553	62
60	1·49807 7	1·49978	1·50061	1·50143	1·50307	1·50473	1·50641 5	1·50812	1·50984	1·51156	1·51330	60
58	1·47664 1	1·47828	1·47910	1·47991	1·48153	1·48316	1·48480 2	1·48646	1·48813	1·48981	1·49150	58
56	1·45570 7	1·45732	1 45813	1·45894	1·46056	1·46218	1·46378 4	1·46536	1·46696	1·46856	1·47013	56
54	1·43515 8	1·43676	1·43756	1·43836	1·43996	1·44154	1·44311 1	1·44467	1·44621	1·44775	1·44929	54
52	1·41505 9	1·41667	1·41747	1·41828	1·41988	1·42145	1·42300 3	1·42454	1·42607	1·42760	1·42914	52
50	1·39543 3	1·39699	1·39778	1·39856	1·40012	1·40169	1·40324 9	1·40480	1·40634	1·40788	1·40942	50
48	1·37623 9	1·37780	1·37857	1·37935	1·38089	1·38244	1·38398 3	1·38553	1·38708	1·38862	1·39017	48
46	1·35748 3	1·35900	1·35976	1·36052	1·36206	1·36360	1·36513 8	1·36669	1·36824	1·36980	1·37136	46
44	1·33910 4	1·34062	1·34138	1·34214	1·34366	1·34520	1·34673 6	1·34828	1·34982	1·35137	1·35293	44
42	1·32115 9	1·32266	1·32342	1·32418	1·32569	1·32719	1·32868 5	1·33021	1·33175	1·33329	1·33485	42
40	1·30349 2	1·39199	1·30575	1·31649	1·30799	1·30949	1·31098 7	1·31251	1·31403	1·31555	1·31709	40
38	1·28616 3	1·28763	1·28837	1·28911	1·29061	1·29211	1·29359 7	1·29508	1·29657	1·29807	1·29957	38
36	1·26909 4	1·27057	1·27131	1·27205	1 27353	1·27501	1·27647 8	1·27794	1·27941	1·28087	1·28233	36
34	1·25227 6	1·25374	1·25446	1·25518	1·25662	1·25808	1·25954 0	1·26100	1·26247	1·26395	1·26542	34

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* 84·5, more accurately 84·4878, the composition of the monohydrate.

TABLE VII—*continued.*

p.	18°.	16°.	15°.	14°.	12°.	10°.	8°.	6°.	4°.	2°.	0°.	p.
32	1·23566 1	1·23708	1·23780	1·23852	1·23998	1·24142	1·24285 6	1·24431	1·24576	1·24721	1·24867	32
30	1·21925 2	1·22067	1·22137	1·22207	1·22348	1·22490	1·22632 4	1·22774	1·22917	1·23061	1·23205	30
28	1·20306 7	1·20445	1·20514	1·20583	1·20721	1·20858	1·20996 0	1·21136	1·21274	1·21414	1·21554	28
26	1·18703 4	1·18837	1·18904	1·18971	1·19105	1·19239	1·19372 8	1·19508	1·19644	1·19782	1·19921	26
24	1·17121 0	1·17250	1·17315	1·17380	1·17510	1·17638	1·17765 5	1·17898	1·18029	1·18161	1·18291	24
22	1·15559 6	1·15682	1·15743	1·15805	1·15929	1·16053	1·16176 5	1·16301	1·16425	1·16549	1·16673	22
20	1·14017 9	1·14135	1·14194	1·14253	1·14370	1·14488	1·14605 0	1·14721	1·14838	1·14955	1·15074	20
18	1·12502 3	1·12612	1·12667	1·12722	1·12832	1·12943	1·13052 7	1·13161	1·13269	1·13377	1·13487	18
16	1·11006 2	1·11110	1·11161	1·11212	1·11314	1·11418	1·11520 4	1·11620	1·11720	1·11821	1·11921	16
14	1·09534 1	1·09633	1·09681	1·09729	1·09824	1·09918	1·10009 7	1·10100	1·10188	1·10276	1·10364	14
12	1·08088 4	1·08178	1·08222	1·08266	1·08352	1·08436	1·08518 1	1·08698	1·08675	1·08749	1·08821	12
10	1·06664 0	1·06746	1·06786	1·06826	1·06904	1·06979	1·07051 8	1·07121	1·07186	1·07247	1·07304	10
8	1·05266 9	1·05341	1·05377	1·05413	1·05482	1·05547	1·05608 2	1·05665	1·05720	1·05771	1·05819	8
6	1·03898 5	1·03961	1·03991	1·04021	1·04080	1·04135	1·04187 0	1·04236	1·04281	1·04320	1·04357	6
5	1·03225 1	1·03285	1·03313	1·03340	1·03391	1·03439	1·03485 8	1·03531	1·03570	1·03602	1·03631	5
4	1·02553 0	1·02607	1·02632	1·02656	1·02702	1·02746	1·02786 9	1·02828	1·02860	1·02886	1·02909	4
3·5	1·02218 1	1·02269	1·02293	1·02316	1·02360	1·02402	1·02441 1	1·02478	1·02510	1·02537	1·02561	3·5
3	1·01885 1	1·01935	1·01958	1·01979	1·02020	1·02060	1·02094 7	1·02126	1·02153	1·02176	1·02197	3
0·5	1·01553 1	1·01598	1·01620	1·01641	1·01680	1·01717	1·01749 4	1·01780	1·01805	1·01824	1·01841	0·5
2·0	1·01222 2	0·01266	1·01286	1·01305	1·01341	1·01375	1·01405 0	1·01432	1·01454	1·01473	1·01479	2·0
1·5	1·00890 3	1·05432	1·00951	1·00969	1·01003	1·01032	0·01057 8	1·01082	1·01102	1·01115	1·01116	1·5
1·0	1·00556 9	1·00594	1·00612	1·00629	1·00659	1·00686	1·00710 7	1·00729	1·00743	1·00760	1·00756	1·0
0·5	1·00221 7	1·00258	1·00273	1·00287	1·00313	1·00337	1·00359 3	1·00383	1·00403	1·00405	1·00400	0·5
0	0·99869 5	0·99903	0·99918	0·99932	0·99956	0·99975	0·99989 0	0·99997	1·00000	0·99997	0·99988	0

TABLE VIIA.—*Densities of Sulphuric Acid Solutions at* 38°, 28°, 18°, *and* 8°.

p.	38°.	28°.	18°.	8°.
99·8	1·814845	1·824760	1·834743	1·845070
99·6	1·815555	1·825497	1·835479	1·845806
99·4	1·816250	1·826186	1·836137	1·846450
99·2	1·816850	1·826766	1·836713	1·847004
98·8	1·817830	1·827626	1·837578	1·847845
98·6	1·818194	1·827936	1·837912	1·848168
98·4	1·818505	1·828191	1·838198	1·848454
98·2	1·818760	1·828396	1·838373	1·848634
96·5	1·818470	1·828151	1·838111	1·848338
93	1·809210	1·819228	1·829431	1·839952
91	1·800024	1·810262	1·820765	1·831459
89	1·718279	1·798706	1·809429	1·820398
87	1·774018	1·984586	1·795526	1·806623
85	1·757434	1·767969	1·778898	1·789912
83	1·738604	1·748901	1·759648	1·770573
81	1·718071	1·728137	1·738544	1·749074
79	1·696232	1·706022	1·716010	1·726197
77	1·673645	1·683189	1·692867	1·702749
75	1·650756	1·659976	1·669457	1·679193
73	1·627562	1·636621	1·645942	1·655397
71	1·604441	1·613325	1·622454	1·631802
69	1·581463	1·590203	1·599193	1·608368
67	1·558715	1·567313	1·576146	1·585178
65	1·536280	1·5447 6	1·553409	1·562266
63	1·514138	1·522393	1·531006	1·539653
61	1·492282	1·500387	1·508963	1·517389
59	1·470823	1·478857	1·487286	1·495538
57	1·449876	1·457806	1·466143	1·474294
55	1·429368	1·427182	1·445384	1·453401
53	1·409313	1·417038	1·425057	1·433042
51	1·389620	1·397281	1·405197	1·413067
49	1·370414	1·379982	1·385774	1·393553
47	1·351623	1·359111	1·366818	1·374521
45	1·333197	1·340614	1·348235	1·355890
43	1·315164	1·322544	1·330112	1·337677
41	1·297453	1·314800	1·312289	1·319801
39	1·280100	1·287358	1·294805	1·302260
37	1·263035	1·270239	1·277611	1·285003
35	1·246256	1·253394	1·260660	1·267979
33	1·229724	1·236768	1·243936	1·251164
31	1·213454	1·220397	1·227424	1·234568
29	1·197410	1·204254	1·211140	1·218116
27	1·181645	1·188302	1·195024	1·201830
25	1·166112	1·172602	1·179104	1·185673
23	1·150802	1·157121	1·163388	1·169687
21	1·135703	1·141819	1·147841	1·153867
19	—	—	1·132576	1·138268
17	—	—	1·117505	1·122834
15	—	—	1·102675	1·107612
13	—	—	1·088071	1·092620
11	—	—	1·073725	1·077813
9	—	—	1·059634	1·063270
7	—	—	1·045788	1·048940
4·5	—	—	1·028890	1·031357

TABLE VIIA—*continued.*

p.	38°.	28°.	18°.	8°.
2·8	—	—	1·017516	1·019565
2·6	—	—	1·016187	1·018185
2·4	—	—	1·014875	1·016803
2·2	—	—	1·013550	1·015420
1·8	—	—	1·010892	1·012665
1·6	—	—	1·009567	1·011271
1·4	—	—	1·008238	1·009884
1·2	—	—	1·006899	1·008498
·8	—	—	1·004247	1·005716
·6	—	—	1·002899	1·004302
·4	—	—	1·001534	1·002884
·3	—	—	1·000844	1·002179
·2	—	—	1·000152	1·001438
·1	—	—	0·999446	1·000678

TABLE VIII.—*Electric Conductivity of Sulphuric Acid Solutions. Direct First and Second Differentiation.*

First differentiation.				Second differentiation.	
p.	$k_{18^\circ}10^8$.	$\frac{dk}{dp}10^8$.	p.	$\frac{d^2k}{dp^2}10^8$.	p.
100·00	0	−355·4	99·72		
*99·44	199	−384·4	99·26	+ 62·2	99·49
*99·08	337·4	−326·7	98·75	−113·1	99·00
*98·42	553	−152·9	97·645	−157·3	98·20
*96·87	790	− 94·6	96·035	− 36·2	96·84
95·20	948	− 33·5	94·05	− 30·8	95·04
92·90	1025	+ 4·6	91·7	− 16·2	92·87
90·50	1014	20·1	89·01	− 5·0	90·35
87·52	954	19·0	86·81	+ 0·5	87·91
86·10	927	+ 8·1	85·295	6·1	86·05
84·49	914	− 12·8	83·275	10·3	84·28
82·06	945	− 48·8	80·38	12·5	81·83
78·70	1109	− 84·3	76·85	10·1	78·61
75·00	1421	−113·6	73·23	8·1	75·04
71·46	1823	−137·9	68·81	5·5	71·02
66·16	2554	−151·4	63·055	2·3	65·93
59·95	3494	−156·5	54·78	+ 0·6	58·92
49·61	5112	−129·4	44·70	− 2·7	49·74
39·79	6383	− 75·9	37·33	− 7·3	41·02
34·87	6784	− 25·6	32·395	− 10·2	34·86
29·92	6911	+ 41·7	27·405	− 13·5	29·90
24·89	6701	121·6	22·42	− 16·0	24·91
19·95	6100	201·7	17·64	− 16·8	20·03
15·33	5168	282·0	12·69	− 16·2	15·16
10·05	3679	344·9	7·535	− 12·2	10·11
5·02	1944	365·7	3·765	− 5·5	5·65
2·51	1026	394·6	1·77	− 14·5	2·77
1·03	443	430·1	0·515	− 28·3	1·14
0	0				

TABLE IX.—*Second Differentiation of Part of the Curve representing the Conductivity of Sulphuric Acid Solutions.*

p.	$\frac{dk}{dp}10^8$.	$\frac{d^2k}{dp^2}10^8$.	p.
0	448·5	−33·0	0·5
1	415·5	−24·0	1·5
2	391·5	−16·0	2·5
3	375·5	−12·5	3·5
4	363·0	− 8·2	4·5
5	354·8	− 5·8	5·5
6	349·0	− 3·2	6·5
7	345·5	− 1·2	7·5
8	344·3	+ 1·2	8·5
9	345·5	+ 3·5	9·5
10	349·0		

TABLE X.—*Determination of the Heat Capacity of Weak Solutions of Sulphuric Acid by dissolving w grams of a* 57·85540 *per cent. solution at* $t° = 14·957°$, *and at* $t'° = 21·051°$, *in* 599·98 *grams of Water.*

$t' - t = 6·092$. *Heat capacity of Water* $= c = 1·005$, $Wc = 602·983$, *Water Equivalent of Apparatus* $= w'c_1 =$ 8·8 *grams, Heat capacity of Strong Acid* $= c' = ·5487$.

Also the first differentiation of the Results.

w.	r at $t°$.	w.	r' at t'.
2·218	·1412	2·200	·1424
2·182	·1386	2·181	·1425
4·097	·2385	3·935	·2349
4·068	·2365	4·310	·2553
7·684	·4124	7·925	·4334
7·676	·4142	8·192	·4446
10·767	·5555	10·284	·5467
12·811	·6498	12·787	·6609
16·834	·8291	16·505	·8310
17·315	·8176	17·319	·8637
21·450	1·0316	21·152	1·0356
23·700	1·1271	23·731	1·1462
29·240	1·3609	29·414	1·3882
29·231	1·3629	29·387	1·3880
34·934	1·6007	34·734	1·6108
34·922	1·6010	34·677	1·6090
35·298	1·6202		
38·721	1·7576	38·294	1·7565
42·067	1·8982	42·636	1·9345
45·725	2·0433	46·174	2·0790
49·756	2·2032	50·473	2·2556
53·704	2·3619	53·596	2·3777
57·242	2·5009	57·761	2·5459

w.	r.	r (mean value).	r'.	r' (mean value).	$r' - r$.	Per cent. H_2SO_4 in the final solution.	c''.	$\frac{dc''}{dp}$.	p.
						0	1·0050		
2·0	·1300	·12958	·1325	·13188	·00230	·19212	1·0031	− ·00989	0. 10
4·0	·2335	·23300	·2385	·23865	·00565	·38317	1·00104	− ·01078	0·29
8·0	·4275	·42797	·4370	·43664	·00867	·76130	·99753	− ·00928	0·57
10·5	·5425	·54336	·5550	·55565	·01229	·99152	·99511	− ·01501	0·88
13·0	·6585	·65783	·6695	·67002	·01219	1·22702	·99330	− ·00769	1·10
17·0	·8350	·83477	·8517	·85160	·01683	1·59417	·98965	− ·00994	1·41
21·5	1·0338	1·03288	1·0505	1·05039	·01751	2·00155	·98634	− ·00813	1 80
24·0	1·1390	1·13902	1·1575	1·15758	·01856	2·22534	·98440	− ·00867	2·11
29·0	1·3518	1·35136	1·3706	1·37043	·01907	2·66758	·98084	− ·00805	2·45
35·0	1·6048	1·60380	1·6215	1·62293	·01913	3·18906	·97672	− ·00790	2·92
38·5	1·7475	1·74790	1·7635	1·76494	·01704	3·48875	·97478	− ·00664	3·34
42·5	1·9145	1·91350	1·9285	1·92922	·01572	3·82724	·97227	− ·00727	3·66
46·0	2·0537	2·05311	2·0725	2·07355	·02044	4·11997	·96920	− ·01049	3·97
50·0	2·2137	2·21285	2·2360	2·23675	·02390	4·45067	·96606	− ·00950	4·28
53·5	2·3526	2·35245	2·3735	2·37498	·02253	4·73672	·96405	− ·00703	4·59
57·5	2·5120	2·51152	2·5340	2·53545	·02393	5·05989	·96125	− ·00863	4·90

TABLE XI.—*Determination of the Heat Capacity of Sulphuric Acid Solution from 5 to 12 per cent., by Dissolving w grams of Acid of 57·89500 per cent. (Heat Capacity, $c' = {\cdot}5487$) in 566·62 grams of Acid of 4·60125 per cent. (Heat Capacity, $c = {\cdot}965$), at $t^\circ = 15{\cdot}002^\circ$, and at $t'^\circ = 20{\cdot}846^\circ$: $t' - t = 5{\cdot}844$: $w'c_1 = 8{\cdot}8$ grams.*

Also the First Differentiation of the Results.

w.	r at t°.	w.	r' at t'°.	w.	r $\left(\text{from } \frac{r}{w}\right)$.	r' $\left(\text{from } \frac{r'}{w}\right)$.	$r' - r$.	Per cent. H_2SO_4 in the final solution.	c''.	$\frac{dc''}{dp}$.	p.
3·266	·1541	3·088	·1477								
2·952	·1421	3·053	·1460					4·60125	·96500		
2·871	·1417	2·961	·1425							− ·00603	4·79
8·541	·4041	8·493	·4077	3·0	·144684	·143781	− ·000903	4·96917	·96278		
8·544	·4067	8·506	·4076		(·141600)		(+ ·002200)		(·96224)		
8·472	·4230	—	—							− ·00812	5·23
11·765	·5554	11·744	·5591	8·5	·403801	·404260	+ ·000459	5·48427	·95860		
11·770	·5562	11·693	·5522			(·407745)	(+ ·003944)		(·95802)		
14·807	·6961	14·163	·6684							− ·00828	5·64
14·672	·6899	15·344	·7229	12·0	·566316	·567900	+ ·001584	5·80687	·95593		
22·746	1·0582	22·459	1·0473							− ·00801	5·94
22·609	1·0534	22·581	1·0532	15·0	·704745	·706905	+ ·002160	6·08024	·95374		
32·983	1·5141	32·893	1·5095							− ·00757	6·44
31·949	1·4695	33·463	1·5346	23·0	1·070420	1·07198	+ ·001564	6·79539	·94833		
42·610	1·9318	41·844	1·8990							− ·00730	7·28
41·960	1·9041	40·756	1·8568	33·0	1·51496	1·51447	− ·000490	7·66205	·94200		
—	—	41·302	1·8724							− ·00753	8·04
—	—	41·908	1·9050	42·0	1·90596	1·90470	− ·00126	8·41728	·93631		
56·677	2·5247	55·428	2·4794							− ·00852	8·98
56·664	2·5272	55·239	2·4701	56·0	2·49833	2·50275	+ ·00442	9·54797	·92668		
73·128	3·1869	70·454	3·0873							− ·00760	10·16
72·196	3·1511	71·225	3·1173	72·0	3·14244	3·14604	+ ·00360	10·77853	·91733		
—	—	72·296	3·1522							− ·00725	11·47
91·665	3·9071	90·269	3·8589	91·0	3·88388	3·88343	− ·00045	12·16084	·90731		
91·714	3·9133	89·611	3·8264								

TABLE XII.—*Heat Capacities of Sulphuric Acid Solutions. Second Differentiation from the Smoothed First Differential Curve.*

p.	$\frac{dc''}{dp}$.	$\frac{d^2c''}{dp^2}$.	p.
9·0	− ·00845		
		− ·00080	8·75
8·5	− ·00805		
		− ·00070	8·25
8·0	− ·00770		
		− ·00040	7·75
7·5	− ·00750		
		0	7·25
7·0	− ·00750		
		+ ·00020	6·75
6·5	− ·00760		
		·00066	6·25
6·0	− ·00793		
		·00050	5·75
5·5	− 00818		
		·00104	5·25
5·0	− ·00870		
		·00090	4·75
4·5	− ·00915		
		+ ·00160	4·25
4·0	− ·00995		
		− ·00620	3·75
3·5	− ·00685		
		+ ·00150	3·25
3·0	− ·00760		
		·00094	2·75
2·5	− ·00807		
		·00090	2·25
2·0	− ·00852		
		·00056	1·75
1·5	− ·00880		
		·00014	1·25
1·0	− ·00887		
		·00440	0·9
0·8	− ·00975		
		·00075	0·7
0·6	− ·00990		
		·00100	0·5
0·4	− ·01010		
		·00125	0·3
0·2	− ·01035		
		·00140	0·1
0	− ·01063		

Table XIII.—*First Differentiation of the Heat Capacity of Solutions of Sulphuric Acid from the Smoothed Curve representing the Determinations.*

p.	c''.	$\frac{dc''}{dp}$.	p.
12·5	·90480		
		− ·00764	12·25
12·0	·90862		
		− ·00734	11·75
11·5	·91229		
		− ·00720	11·25
11·0	·91589		
		− ·00732	10·75
10·5	·91955		
		− ·00736	10·25
10·0	·92328		
		− ·00744	9·75
9·5	·92695		
		− ·00882	9·25
9·0	·93137		
		− ·00782	8·75
8·5	·93528		
		− ·00774	8·25
8·0	·93915		
		− ·00776	7·75
7·5	·94303		
		− ·00764	7·25
7·0	·94685		
		− ·00770	6·75
6·5	·95070		
		− ·00764	6·25
6·0	·95452		
		− ·00750	5·75
5·5	·95827		
		− ·00736	5·25
5·0	·96195		
		− ·00776	4·75
4·5	·96583		
		− ·00982	4·25
4·0	·97075		
		− ·00700	3·9
3·8	·97215		
		− ·00690	3·7
3·6	·97359		
		− ·00735	3·5
3·4	·97506		
		− ·00755	3·3
3·2	·97659		
		− ·00775	3·1
3·0	·97812		
		− ·00785	2·9
2·8	·97969		
		− ·00800	2·7
2·6	·98129		
		− ·00815	2·5
2·4	·98292		
		− ·00835	2·3
2·2	·98459		
		− ·00850	2·1
2·0	·98629		
		− ·00870	1·9
1·8	·98803		
		− ·00870	1·7
1·6	·98977		
		− ·00890	1·5
1·4	·99155		
		− ·00895	1·3
1·2	·99334		
		− ·00910	1·1
1·0	·99516		
		− ·00995	0·9
·8	·99715		
		− ·00930	0·7
·6	·99901		
		− ·00960	0·5
·4	1·00093		
		− ·01000	0·3
·2	1·00293		
		− ·01035	0·1
0	1·00500		

TABLE XIV.—*Heat evolved on Mixing Solutions of Sulphuric Acid with Water at* 17·91° ± ·01.
Water used (W) = 419·47 *grams*, $w'' = W + w$; $w'c_1 = 21·74$ *grams.*

p.	w.	$(t'-t)°$.	p'.	c''.	$w''c''$.	$w''c'' + w'c_1$.	D^{100} obs.		Correction for infinity.	D^{100}_{∞} approx.	Correction due to p'.	D^{100}_{∞} corr.	$\frac{D^{100}_{\infty}}{p}$.
First Series.													
17·83046	472·16	0·2628 0·2644	9·44212	0·92783	827·28	850·36	47·321 47·623	47·472	655·866	703·338	−0·315	703·023	39·428
17·83046	471·41	0·2495 0·2496	9·43500	0·92780	826·56	849·64	44·976 45·007	44·991	656·357	701·348	−0·826	700·522	39·288
9·44272	446·10	0·0874 0·0872	4·86661	0·96300	833·54	856·62	16·781 16·747	16·764	330·548	349·312	−0·136	347·176	36·767
4·86949	432·60	0·0548 0·0531	2·47226	0·98233	837·01	860·09	10·907 10·565	10·736	159·623	170·359	+0·044	170·403	34·994
2·47354	426·85	0·0341 0·0346	1·24755	0·99293	840·34	863·42	6·8939 7·0092	6·9515	74·090	81·0415	+0·022	81·0635	32·789
1·24755	422·19	0·0247 0·0255	0·62563	0·99878	840·63	863·71	5·0455 5·2335	5·1395	32·2285	—	—	37·368	29·957
0·62563	420·66	0·0143 0·0146	0·31326	1·00183	841·67	864·75	2·9342 3·0119	2·9731	13·189	—	—	16·162	25·833
0·31326	420·47	0·0091 0·0092	0·15681	1·00333	842·78	865·86	1·8795 1·8917	1·8856	4·7182	—	—	6·6038	21·08
0·15681	419·79	0·0065 0·0060	0·07844	1·00418	842·77	865·85	1·2417 1·3431	1·2924	1·0695	—	—	2·3619	15·06
0·07844	420·00	0·0010 0·0016	0·03924	1·04585	877·96	901·04	2·0831 3·4925	2·7878	0·25615	—	—	0·5349	6·82
0·03924	—	—	0	for 1·004585 —	—	—	for 0·26806 —		0·12816	—	—	0·12816	3·26
Second Series.													
6·78193	438·38	0·0592 0·0590	3·46571	0·97463	836·09	859·17	11·608 11·554	11·581	229·828	241·409	+0·142	241·551	35·617
3·46457	429·03	0·0456 0·0451	1·75180	0·98849	838·73	861·81	9·1672 9·0628	9·115	108·332	117·447	+0·006	117·453	33·901
1·75170	424·19	0·0341 0·0311	0·88075	0·99633	842·56	865·64	6·9224 6·3060	6·6142	48·162	54·776	−0·001	54·775	33·270
0·88077	421·06	0·0172 0·0181	0·44122	1·00053	840·98	864·06	3·5268 3·7225	3·6247	20·591	—	—	24·216	27·494
0·44122	420·24	0·0101 0·0106	0·22081	1·00273	842·00	865·08	2·0787 2·1782	2·1285	8·1865	—	—	10·315	23·378
0·22081	420·30	0·0087 0 0073	0·11051	1·00388	843·03	866·11	1·8008 1·5096	1·6552	2·4418	—	—	4·0970	18·556
0·11051	419·51	0·0028 0·0037	0·05526	1·0441	875·98	899·06	0·6035 0·7975	0·7005	0·5217	—	—	1·2221	11·06
0·05526	—	—	0	for 1·0041 —	—	—	for 0·67452 —		0·26083	—	—	0·26083	4·72

TABLE XV.—*Heat of Dissolution of Sulphuric Acid Solutions at* 17·91° ± 0·01. *Water used* = 599·983 *grams*, $w'c_1$ = 8·83 *to* 8·66 *grams*, w'' = 599·983 + w.

p.	w.	$(t'-t)^\circ$.	p'.	c''.	$w''c''$.	$w''c''+w'c_1$.	D^{100} obs.	Correction for infinity.	D^{100}_α		$\frac{dD}{dp}$.	p.
											Alternate dets.	
99·8500	6·0445	1·8358	0·9959	·99532	603·19	611·85	18583	2847	21430	21425 A		
,,	6·6502	2·0115	1·0946	·99437	603·21	611·87	18507	2914	21422			
,,	6·7513	2·0413	1·1111	·99420	603·21	611·87	18500	2922	21422			
99·7838	5·2643	1·6019	0·86789	·99651	603·14	611·80	18617	2757	21374	21371 B	547 A	99·63
,,	5·7570	1·7450	0·94834	·99576	603·17	611·83	18545	2810	21355			
,,	5·8940	1·7876	0·97070	·99554	603·18	611·84	18557	2827	21384			
99·5181 (2)	4·3486	1·3236	0·7161	·99793	603·08	611·74	18619	2618	21237	21243·5 A	619 B	99·44
,,	4·2060	1·2826	0·6927	·99814	603·07	611·73	18654	2596	21250			
99·0937 (2)	6·0585	1·7950	0·99055	·99536	603·23	611·89	18129	2821	20950	20943·5 B	707 A	99·15
,,	6·7199	1·9815	1·0975	·99434	603·26	611·92	18044	2893	20937			
98·7781 (2)	6·6204	1·9317	1·0780	·99452	603·28	611·94	17936	2775	20711	20720·5 A	651 B	98·44
,,	6·6142	1·9302	1·0770	·99453	603·28	611·88	17857	2873	20730			
97·7882 (2)	4·8754	1·3909	0·7882	·99728	603·22	611·88	17457	2632	20089	20093 B	632 A	97·99
,,	4·4702	1·2800	0·7231	·99787	603·16	611·82	17518	2579	20097			
97·1924	6·2830	1·7374	1·0072	·99520	603·36	612·02	16924	2780	19704	19719 A	628 B	96 93
,,	6·5407	1·8082	1·0481	·99481	603·37	612·03	16919	2815	19734			
,,	6·8606	1·8919	1·0988	·99432	603·39	612·05	16878	2840	19718			
95·8763 (2)	6·3577	1·6779	1·0052	·99479	603·18	611·84	16147	2742	18889	18893 B	627 A	96·04
,,	6·3727	1·6819	1·0076	·99520	603·46	612·12	16155	2742	18897			
94·8949	6·4129	1·6312	1·0035	·99523	603·51	612·17	15571	2712	18283	18278 A	604 B	94·89
,,	6·2086	1·5798	0·9719	·99554	603·49	612·15	15576	2687	18263			
,,	6·4400	1·6383	1·0077	·99520	603·51	612·17	15573	2716	18289			
93·9051 (2)	7·1524	1·7448	1·1063	·99426	605·05	613·71	14970	2744	17714	17702·5 B	607 A	93·72
,,	6·4171	1·5707	0·9937	·99533	604·96	613·62	15016	2675	17691			
92·5471	6·7066	1·5548	1·0231	·99504	603·68	612·34	14196	2662	16858	16853 A	618 B	92·88
,,	7·2825	1·6814	1·1098	·99423	603·77	612·43	14140	2708	16848			

TABLE XV—*continued.*

p.	w.	$(t'-t)^\circ$.	p'.	c''.	$w''c''$.	$w''c''+w'c_1$.	D^{100} obs.	Correction for infinity.	D^{100}_{∞}.			$\frac{dD}{dp}$.		p.
												Alternate dets.		
91·8662 (2)	7·6554	1·7156	1·1573	·99378	603·86	612·52	13727	2708	16435	16441·5	B	606	A	91·78
,,	7·4176	1·6659	1·1218	·99410	603·82	612·48	13756	2692	16448					
91·0247 (2)	8·8394	1·9009	1·3215	·99228	604·12	612·78	13178	2739	15917	15931	A	596	B	91·12
,,	7·9070	1·7104	1·1839	·99354	603·96	612·62	13253	2693	15945					
90·3750	8·2540	1·7333	1·2265	·99315	604·07	612·73	12867	2690	15557	15552·5	B	568	A	90·03
,,	7·7055	1·6211	1·1460	·99388	603·97	612·63	12889	2659	15548					
89·0310 (2)	8·1677	1·6211	1·1956	·99342	604·15	612·83	12163	2638	14801	14799	A	554	B	89·34
,,	6·9358	1·3860	1·0174	·99510	603·95	612·63	12242	2555	14797					
88·2980	7·1391	1·3824	1·0383	·99490	604·02	612·70	11864	2550	14414	14402	B	542	A	88·03
,,	6·9305	1·3418	1·0088	·99520	604·00	612·68	11862	2528	14390					
87·0362 (2)	7·2725	1·3300	1·0423	·99487	604·15	612·83	11207	2518	13725	13717·5	A	534	B	87·24
,,	7·0664	1·2973	1·0313	·99515	604·11	612·79	11215	2495	13710					
86·1863	9·0260	1·5701	1·2778	·99266	604·54	613·22	10692	2582	13274	13274	B	495	A	86·00
,,	8·4737	1·4812	1·2003	·99337	604·41	613·09	10717	2557	13274					
84·9791 (2)	7·5783	1·2661	1·0599	·99470	604·34	613·02	10241	2467	12708	12698·5	A	482	B	85·09
,,	6·7827	1·1393	0·9499	·99574	604·19	612·87	10294	2395	12689					
84·0197 (2)	8·6524	1·3748	1·1949	·99340	604·61	613·26	9744	2491	12235	12230	B	449	A	83·99
,,	10·8926	1·7111	1·4988	·99066	605·16	613·84	9643	2582	12225			463	A′	83·98
83·0117 (2)	8·4082	1·2855	1·1472	·99386	604·65	613·33	9377	2442	11819	11815	A			
,,	6·3466	0·9856	0·8689	·99652	604·22	612·90	9517	2294	11811					
82·9927	9·9196	1·4976	1·3498	·99202	605·03	613·80	9267	2507	11774	11779	A′	424	B	82·94
,,	9·3407	1·4155	1·2723	·99270	604·87	613·64	9299	2484	11784					
81·8501 (2)	7·4067	1·0843	0·9980	·99526	604·51	613·19	8977	2334	11311	11310	B	426	A	82·00
,,	9·0729	1·3123	1·2192	·99320	604·91	613·59	8875	2434	11309			412	A′	81·99
80·9875	8·8076	1·2290	1·1717	·99866	604·98	613·61	8562	2891	10958	10953	A	395	B	80·91
,,	8·9415	1·2466	1·1892	·99347	604·94	613·62	8555	2398	10953					

TABLE XV—*continued.*

p.	w.	$(t'-t)^\circ$.	p'.	c''.	$w''c''$.	$w''c''+w'c_1$.	D^{100} obs.	Correction for infinity.	D^{100}_{α}.			$\frac{dD}{dp}$.		p.
												Alternate dets.		
79·9681 (2)	9·3886	1·2530	1·2320	·99310	605·17	613·87	8192	2381	10578	10567·5	B	879	A	79·98
„	12·9973	1·7036	1·6955	·98894	606·20	614·90	8060	2502	10562			849	A′	79·87
78·9900 (2)	9·7204	1·2407	1·2592	·99282	605·32	614·02	7836	2360		10196	A			
78·7547	11·7938	1·4882	1·5182	·99048	605·96	614·66	7756	2424	10130	10174·5	A′	351	B	78·57
„	11·4747	1·4476	1·4779	·99084	605·86	614·56	7753	2416	10169					
77·1791	11·9868	1·4069	1·5117	·99055	606·19	614·89	7217	2373	9590	95895	B	323	A	77·44
„	11·1388	1·3126	1·4067	·99150	605·93	614·63	7243	2346	9589			342	A′	77·33
75·9072 (2)	10·7821	1·2119	1·3399	·99213	605·96	614·69	6909	2289	9198	91995	A	318	B	76·09
„	9·4882	1·0744	1·1816	·99355	605·54	614·24	6956	2246	9201					
75·0013	12·4940	1·3380	1·5300	·99039	606·59	615·29	6589	2311	8900	8897	B	318	A	74·97
„	12·0207	1·2900	1·4732	·99087	606·41	615·11	6595	2299	8894			301	A′	74·94
74·0417	14·9857	1·5240	1·8043	·98800	607·57	616·29	6267	2336	8603	8606	A	288	B	73·51
„	12·8268	1·3177	1·5498	·99020	606·80	615·50	6323	2286	8609					
73·9864 (2)	9·6883	1·0147	1·1756	·99360	605·77	614·47	6435	2187		8622	A′			
72·0223 (2)	7·4586	0·7342	0·8844	·99637	605·24	613·94	6043	1996	8039	8040·5	B	278	A	72·58
„	10·8939	1·0422	1·2845	·99260	606·36	615·06	5883	2159	8042			289	A′	72·55
71·1257	15·7316	1·4141	1·8172	·98786	608·23	616·93	5546	2245	7791	7795	A	258	B	70·02
„	14·1996	1·2861	1·6444	·98938	607·66	616·36	5583	2216	7799					
68·0085 (2)	11·7437	0·9463	1·3055	·99244	607·11	615·83	4963	2042	7005	7006	B	250	A	68·54
„	10·8696	0·8808	1·2101	·99329	606·75	615·47	4987	2020	7007					
65·9711	21·378	1·5054	2·2699	·98404	611·44	620·16	4367	2142	6509	6504	A	227	B	66·03
„	22·742	1·5931	2·4093	·98285	612·04	620·76	4349	2158	6507					
„	29·568	2·0275	3·0984	·97734	615·28	624·00	4279	4216	6495					
64·0454 (2)	11·2840	0·7724	1·1822	·99355	607·33	616·07	4217	1894	6111	6105·5	B	211	A	63·63
„	12·6730	0·8575	1·3247	·99226	607·92	616·64	4172	1928	6100					
61·2986	25·472	1·4346	2·4965	·98211	614·26	622·98	3509	2015	5524	5518	A	203	B	62·01
„	26·287	1·4722	2·5729	·98150	614·68	623·40	3491	2023	5514					
„	23·954	1·3540	2·3533	·98332	613·53	622·25	3517	2000	5517					

TABLE XV—*continued.*

p.	w.	$(t'-t)°$.	p'.	c''.	$w''c''$.	$w''c''+w'c_1$.	D^{100} obs.	Correction for infinity.	D^{100}_{∞}.		$\frac{dD}{dp}$.	p.
											Alternate dets.	
59·9705 (2)	15·7950	0·8755	1·5382	·99033	609·83	618·57	3429	1850	5279	5276·5 B	189 A	59·57
”	18·4438	1·0085	1·7843	·98818	611·12	619·86	3389	1885	5274			
57·8568	25·010	1·1974	2·3153	·98364	614·77	623·51	2985	1884	4869	4867·5 A	183 B	57·99
”	26·490	1·2596	2·4461	·98257	615·55	624·29	2968	1898	4866			
56·0091 (2)	17·466	0·7942	1·5842	·98992	611·23	619·97	2819	1736	4555	4553 B	171 A	55·68
”	19·280	0·8669	1·7437	·98853	612·16	620·90	2792	1759	4551			
53·5069	24·903	0·9574	2·1324	·98520	615·63	624·37	2400	1725	4125	4124·5 A	161 B	54·02
”	28·370	1·0748	2·4158	·98280	617·54	626·28	2373	1751	4124			
52·0268 (2)	16·932	0·6351	1·4278	·99132	611·73	620·30	2327	1586	3918	3913 B	151 A	51·55
”	17·232	0·6454	1·4524	·99110	611·56	620·47	2323	1590	3913		152 A′	51·38
49·59205	29·256	0·8937	2·3055	·98374	619·00	627·76	1918	1613	3531	3533·5 A	148 B	50·03
”	25·689	0·7993	2·0362	·98603	616·93	625·63	1947	1589	3536			
49·2519	38·181	1·1027	2·9468	·97854	624·47	633·23	1829	1647	3476	3477·5 A′		
”	34·756	1·0170	2·6970	·98052	622·38	631·14	1847	1632	3479			
48·0265 (2)	18·594	0·5551	1·4435	·99116	613·11	621·87	1857	1466	3323	3322·5 B	136 A	47·65
”	16·623	0·5037	1·2946	·99250	611·98	620·74	1881	1441	3322		133 A′	47·49
45·7167 (2)	27·563	0·6793	2·0078	·98624	618·92	627·68	1543	1463	3006	3005·5 A	129 B	45·80
”	24·865	0·6204	1·8191	·98786	617·26	626·05	1562	1443	3005			
43·5898 (2)	15·339	0·3658	1·0865	·99446	611·91	620·67	1480	1269	2749	2749 B	121 A	43·74
”	17·259	0·4053	1·2256	·99316	613·12	621·88	1452	1297	2749			
41·7674 (2)	19·923	0·4061	1·3422	·99207	614·99	623·75	1271	1261	2532	2529·5 A	110 B	41·62
”	21·855	0·4367	1·4678	·99096	616·22	624·98	1249	1278	2527			
39·6478 (2)	18·674	0·3366	1·1967	·99341	614·58	623·35	1124	1174	2298	2294·5 B	108 A	39·75
”	21·396	0·3737	1·3651	·99188	616·33	625·10	1092	1199	2291			
37·7311 (2)	22·112	0·3395	1·3410	·99210	617·19	625·96	961	1138	2099	2094·5 A	101 B	37·68
”	22·760	0·3439	1·3789	·99174	617·60	626·37	947	1143	2090		103 B′	37·61

TABLE XV—*continued.*

p.	w.	$(t'-t)^\circ$.	p'.	c''.	$w''c''$.	$w''c''+w'c_1$.	D^{100} obs.	Correction for infinity.	D^{100}_∞.			$\frac{dD}{dp}$.	p.
												Alternate dets.	
35·7188 (2)	25·458	0·3269	1·4538	·99107	619·86	628·63	807	1092		1899	B		
35·5663	29·627	0·3604	1·6736	·98914	622·77	631·54	772	1112	1884	1874	B′	90·6 A	35·79
”	40·834	0·4588	2·2681	·98406	631·57	640·34	720	1144	1864				
33·8520 (2)	23·637	0·2739	1·2830	·99260	619·01	627·78	728	1015	1743	1743	A	85·1 B	33·88
”	23·052	0·2692	1·2524	·99289	618·60	627·37	732	1011	1743			81·7 B′	33·80
32·0398	33·722	0·3100	1·7049	·98887	626·67	635·44	584	1004	1588	1586	B	78·5 A	31·55
”	36·918	0·3301	1·8572	·98748	628·93	637·70	570	1015	1585				
”	27·591	0·2669	1·4090	·99148	622·22	630·99	609	975	1584				
29·2423	36·961	0·2755	1·6969	·98890	629·88	638·66	476	915	1391	1381	A	73·1 B	29·90
”	35·469	0·2598	1·6322	·98951	628·79	637·57	467	910	1377				
”	30·704	0·2348	1·4236	·99137	625·25	634·03	485	891	1376				
27·7528 (2)	26·234	0·1887	1·1625	·99372	622·29	631·07	454	819	1273	1272·5	B	66·7 A	27·40
”	31·000	0·2112	1·3634	·99188	625·86	634·64	432	840	1272				
25·5694	38·988	0·2082	1·5620	·99011	632·65	641·43	343	790	1133	1136	A	61·8 B	25·79
”	31·195	0·1835	1·2637	·99278	626 62	635·40	374	765	1139				
23·8370 (2)	24·454	0·1389	0·9334	·99588	621·87	630·65	358	669	1027	1030·5	B	58·3 A	23·88
”	22·397	0·1340	0·8577	·99660	620·26	629·04	377	657	1034			59·8 A′	23·74
22·1891	27·862	1·3468	0·9847	·99540	624·96	633·74	306	631	937	939	A	55·3 B	21·84
”	37·547	1·6041	1·3068	·99242	632·70	641·48	274	667	941				
21·9229 (2)	26·061	0·1259	0·9112	·99610	624·49	633·27	306	611	917	918	A′		
”	25·727	0·1259	0·9013	·99617	623·31	632·09	310	609	919				
19·8413 (2)	21·632	0·1004	0·6904	·99816	620·48	629·28	292	517	809	809·5	B	51·3 A	20·18
”	20·729	0·0985	0·6626	·99841	619·72	628·52	298	512	810			49·3 A′	20·05
18·1835 (2)	27·504	0·1043	0·7970	·99716	625·70	634·50	240	491	731	733·5	A	47·6 B	17·99
”	27·896	0·1070	0·8078	·99709	626·05	634·85	243	493	736				
16·1315 (2)	23·305	0·0839	0·6032	·99898	622·66	631·46	227	405	632	633	B	45·6 A	16·10
”	24·271	0·0861	0·6272	·99874	623·46	632·26	224	410	634				

TABLE XV—*continued*.

p.	w.	$(t'-t)°$.	p'.	c''.	$w''c''$.	$w''c''+w'c_r$	D^{100} obs.	Correction for infinity.	D^{100}_{α}.		$\frac{dD}{dp}$.	p.
											Alternate dets.	
14·0271 (2)	24·707	0·0778	0·5548	·99943	624·34	633·14	199	346	545	544 A	42·4 B	14·07
,,	24·972	0·0772	0·5605	·99936	624·55	633·35	196	347	543			
12·0073 (2)	26·982	0·0706	0·5167	·99979	626·83	635·63	167	290	457	458 B	40·5 A	12·08
,,	27·973	0·0727	0·5349	·99960	627·70	636·50	165	294	459		40·3 A′	12·02
10·0378	30·016	0·0662	0·4782	1·00015	630·09	638·89	141·4	238·4	279·4	382·6 A	38·6 B	10·47
,,	29·622	0·0686	0·4723	1·00024	629·76	638·56	148·0	237·8	285·8			
10·0113 (2)	27·395	0·0642	0·4371	1·00057	627·74	636·54	149·2	232·3		381·5 A′		
8·9703 (2)	22·925	0·0551	0·3301	1·00166	623·94	632·74	151·0	192·6	344·6	346·1 B	36·6 A	9·15
,,	22·441	0·0552	0·3234	1·00170	623·48	632·28	155·7	191·8	347·5		37 0 A′	9·14
8·2660	27·541	0·0570	0·3628	1·00134	628·36	637·16	131·0	183·0	314·9	—	36·5 B	7·97
,,	28·522	0·0605	0·3751	1·00117	629·25	638·05	135·4	184·3	319·7	317·7 A′	38·7 B′	7·83
,,	25·941	0·0567	0·3426	1·00153	626·88	635·68	139·0	179·6	318·6	—		
6·9622 (2)	22·400	0·0454	0·2506	1·00246	623·91	632·71	128·4	133·9	262·3	262·8 B	43·3 A	7·22
,,	22·958	0·0462	0·2566	1·00240	624·44	633·24	127·5	135·7	263·2			
6·6981	22·204	0·0470	0·2390	1·00256	623·78	632·58	133·9	126·9	260·8	258·1 B′	41·8 A′	7·09
,,	23·333	0·0465	0·2507	1·00247	624·86	633·66	126·3	129·0	255·3			
6·1461	26·928	0·0450	0·2640	1·00230	628·35	637·15	106·4	121·6	228·0	228·0 A	38·9 B	5·94
,,	29·687	0·0472	0·2898	1·00208	630·98	639·28	101·6	126·3	227·9			
5·9214 (2)	26 387	0·0429	0·2494	1·00248	627·92	636·72	103·5	114·2	217·7	219·8 A′	42·1 B′	5·81
,,	26·907	0·0450	0·2541	1·00240	628·39	637·18	106·5	115·4	221·9			
4·9159 (2)	31·133	0·0420	0·2425	1·00253	632·72	641·52	86·6	93·8	180·4	183·1 B		
,,	31·867	0·0452	0·2479	1 00249	633·42	642·22	91·0	94·7	185·7			

Those solutions marked (2) belonged to the C series of preparations (p. 73); the others to the A series.

Table XVI.—***Heat of Dissolution of Sulphuric Acid***
***Differentiation of the** Smoothed Curve representing the Re*

First differentiation.				Second differentiation		
p.	D.	$\frac{dD}{dp}$.	*p.*	*p.*	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.
99·5	21215	676	99·25	99·4	680	35
99·0	20877	660	98·75	99·0	666	30
98·5	20547	646	98·25	98·6	654	27·5
98·0	20224	634	97·75	98·2	643	22·5
97·5	19907	610	97·25	97·8	634	20·0
97·0	19602	630	96·75	97·4	626	−11
96·5	19287	634	96·25	96·75	634	14
96·0	18967	626	95·75	96·25	627	16
95·5	18657	614	95·25	95·75	619	18
95·0	18350	600	94·75	95·25	610	24
94·5	18050	592	94·25	94·75	600	22
94·0	17754	626	93·75	94·25	589	−144
93·5	17441	628	93·25	94·0	625	4
93·0	17127	604	92·75	93·5	623	8
92·5	16825	620	92·25	93·0	619	14
92·0	16515	600	91·75	92·5	612	14
91·5	16215	596	91·25	92·0	605	20
91·0	15917	578	90·75	91·5	595	24
90·5	15628	556	90·25	91·0	583	28
90·0	15350	566	89·75	90·5	569	30
89·5	15067	568	89·25	90·0	554	−50
89·0	14783	552	88·75	89·5	579	34
88·5	14507	544	88·25	89·0	563	30
88·0	14235	528	87·75	88·5	548	26
87·5	13971	530	87·25	88·0	535	24
87·0	13707	514	86·75	87·5	523	18
86·5	13450	500	86·25	87·0	514	18
86·0	13200	490	85·75	86·5	505	14
85·5	12955	496	85·25	86·0	498	12
85·0	12707	484	84·75	85·5	492	6
84·5	12465	466	84·25	85·0	489	2
84·0	12232	439	83·5	84·5	488	47
83	11793	428	82·5	83·5	441	15
82	11365	408	81·5	82·5	426	17
81	10957	392	80·5	81·5	409	18·5
80	10565	368	79·5	80·5	390·5	22
79	10197	332	78·5	79·5	368·5	24
78	9865	335	77·5	78·5	334·5	
77	9530	310	76·5			9·0
76	9222	312	75·5	73·5	290·5	6·5
75	8910	295	74·5	72·5	284·0	10·0
74	8615	292	73·5	71·5	274·0	9·5
73	8323	286	72·5	70·5	264·5	9·0
72	8037	272	71·5	69·5	255·5	9·0
71	7765	268	70·5	68·5	246·5	7·5
70	7497	—	69·5	67·5	239·0	8·0
69	7237	245	68·5	66·5	231 0	9·7
68	6992			65·5	223·3	

TABLE XVI—*continued.*

First differentiation.				Second differentiation.			
p.	D.	$\frac{dD}{dp}$.	p.	p.	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p.
68	6992			65·5	223·3		
		235	67·5			6·3	65
67	6757			64·5	217·0		
		232	66·5			6·5	64
66	6525			63·5	210·5		
		282	65·5			7·0	63
65	6303			62·5	203·5		
		216	64·5			6·0	62
64	6087			61·5	197·5		
		212	63·5			5·5	61
63	5875			60·5	192·0		
		207	62·5			2·6	60·25
62	5668						
		195	61·5	60·0	190·7		
61	5473					4·97	60 to 51
		193	60·5				
60	5280			51·0	146·0		
						4 0	50·25
	5271			49·5	140·0		
		189	59·5				
59	5082					3·23	49·5 to 36·5
		185	58·5				
58	4897						
		179	57·5	36·5	98·0		
57	4718					7·2	35·75
		172	56·5				
56	4548			35	87·2		
		168	55·5			3·3	34·5
55	4378			34	83·9		
		165	54·5			3·1	33·5
54	4213			33	80·8		
		160	53·5			2·9	31·5
53	4053			32	77·9		
		155	52·5			2·5	31·5
52	3898			31	75·4		
		147	51·5			2·2	30·5
51	3751			30	73·2		
		166	50·5			1·9	29·5
50	3585			29	71·3		
		141	49·5			5·6	28·5
49	3444			28	65·7		
		138	48·5				
48	3306					4·13	28 to 20
		134	47·5				
47	3172			20	32·7		
		129	46·5			−11·5	19·25
46	3043			18·5	50·0		
		126	45·5			1·5	18
45	2917			17·5	48·5		
		124	44·5			1·5	17
44	2793			16·5	47·0		
		121	43·5			1·6	16
43	2672			15·5	45·4		
		117	42·5			1·6	15
42	2557			14·5	43·8		
		114	41·5			1·6	14
41	2441			13·5	42·2		
		111	40·5			1·8	13
40	2330			12·5	40·4		
		108	39·5			1·7	12
39	2222			11·5	38·7		
		104	38·5			1·8	11
38	2118			10·5	36·9		
		101	37·5			−4·2	9·63
37	2017			8·75	44·2		
		99	36·5			2·6	8·5
36	1918			8·25	42·9		
		86·8	35·5			2·4	8·0
35	1831·5			7·75	41·7		
		84·5	34·5			2·0	7·5
34	1747·0			7·25	40·7		
		83·5	33·5			1·2	7·0
33	1663·5			6·75	40·1		
						1·0	6·5
				6·25	39·6		
						0·6	6·0
				5·75	39·3		
						0·2	5·5
				5·25	39·2		

TABLE XVI—*continued.*

First differentiation.			
p.	D.	$\frac{dD}{dp}$	p.
33	1663·5		
		78·3	32·5
32	1585·2		
		77·0	31·5
31	1508·2		
		73·5	30·5
30	1434·7		
		73·0	29·5
29	1361·7		
		72·2	28·5
28	1289·5		
		64·2	27·5
27	1225·3		
		63·6	26·5
26	1161·7		
		60·7	25·5
25	1101·0		
		61·5	24·5
24	1039·5		
		57·5	23·5
23	982·0		
		56·0	22·5
22	926·0		
		55·0	21·5
21	871·0		
		53·5	20·5
20	817·5		
		33·5	19·5
19	774·0		
		50·0	18·5
18	724·0		
		48·5	17·5
17	675·5		
		46·8	16·5
16	628·7		
		44·7	15·5
15	584·0		
		44·0	14·5
14	540·0		
		41·8	13·5
13	498·2		
		41·0	12·5
12	457·2		
		38·5	11·5
11	418·7		
		37·7	10·5
10	381·0		
		32·7	9·5
9	348·3		
		44·6	8·75
8·5	326·0		

First differentiation.			
p.	D.	$\frac{dD}{dp}$.	p.
8·5	326·0		
		42·4	8·25
8·0	304·8		
		42·0	7·75
7·5	283·8		
		40·6	7·25
7·0	263·5		
		40·0	6·75
6·5	243·5		
		39·0	6·25
6·0	224·0		
		40·0	5·75
5·5	204·0		
		39·0	5·25
5·0	185·0		
Another reading.			
46	3042		
		122	45·5
45	2920		
		118	44·5
44	2802		
		121	43·5
43	2681		
		118	42·5
42	2563		
		114	41·5
41	2449		
		113	40·5
40	2336		
		109	39·5
39	2227		
		106	38·5
38	2121		
		103	37·5
37	2018		
		92	36·5
36	1926		
		92	35·5
35	1834		
		87	34·5
34	1747		
		84	33·5
33	1663		
		79	32·5
32	1582		
		76	31·5
31	1506		
		70	30·5
30	1436		
		70	29·5
29	1366		

TABLE XVII.—*Heat of Dissolution of Sulphuric Acid Solutions. First Differentiation of the Ultra-smoothed Curve representing the Results.*

p.	D.	$\frac{dD}{dp}$.	*p*.	*p*.	D.	$\frac{dD}{dp}$.	*p*.
100	24555	670	99·5	70	7505	260	69
99	20885	645	98·5	68	6995	255	67
98	20240	640	97·5	66	6527	234	65
97	19590	643	96·5	64	6088	220	63
96	18957	622	95·5	62	5671	209	61
95	18335	620	94·5	60	5274	199	59
94	17715	607	93·5	58	4902	175	57
93	17108	588	92·5	56	4553	168	55
92	16520	587	91·5	54	4217	158	53
91	15933	570	90·5	52	3902	151	51
90	15363	570	89·5	50	3600	144	49
89	14793	543	88·5	48	2313	129	47
88	14250	545	87·5	46	3055	128	45
87	13705	515	86·5	44	2800	123	43
86	13190	487	85·5	42	2555	113	41
85	12703	463	84·5	40	2330	104	59
84	12240	450	83·5	38	2123	98	37
83	11790	425	82·5	36	1927	92	35
82	11365	405	81·5	34	1743	79	33
81	10960	395	80·5	32	1585	74	31
80	10565	370	79·5	30	1438	69	29
79	10195	345	78·5	28	1300	69	27
78	9850	337	77·5	26	1163		
77	9513	313	76·5				
76	9200	293	75·5	46	3049	129	45
75	8907	292	74·5	44	2791	120	43
74	8615	302	73·5	42	2552	112	41
73	8313	278	72·5	40	2329	104	39
72	8035	270	71·5	38	2121	96	37
71	7765	260	70·5	36	1929	90·5	35
70	7505	258	69	34	1748	82·5	33
68	7000	238	67	32	1583	76	31
66	6525	220	65	30	1431	71	29
64	6085	205	63	28	1289	65	27
62	5675			26	1159	60	25
				24	1039	57	23
78	9877	328	77·5	22	926	53	21
77	9540	324	76·5	20	820	49	19
76	9225	315	75·5	18	722	47	17
75	8910	303	74·5	16	629	44	15
74	8607	287	73·5	14	541	41	13
73	8328	283	72·5	12	460	38	11
72	8037	272	71·5	10	384	35	9
71	7765	272	70·5	8	314		
70	7505						

TABLE XVIII.—*Heat of Dissolution of Sulphuric Acid Solutions. Second Differentiation from the Smoothed First Differential Curve.*

p.	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p.	p.	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	p.
99·6	547	−600	99·4	55	165·5	+4·0	54·5
99·2	695	+ 48	98·6	54	161·5	4·0	53·5
98	637	+ 8·56	98 to 94	53	157·5	3·5	52·5
94	602·7	− 12	93·5	52	154	4·0	51·5
93	614·7	+ 8·7	92·5	51	150	4·0	50·5
92	606	15·5	91·5	50	146	6·0	49·5
91	590·5	23·0	90·5	49	140	3·05	49 to 39
90	567·5	+ 30·5	89·5	39	109·5	7·8	38·5
89	537	− 5·7	88·5	38	101·7	4·5	37·5
88	542·7	+ 21·4	88 to 80	37	97·2	4·9	36·5
80	371·5	15·5	79·5	36	92·3	4·3	35·5
79	356	14	78·5	35	88·0	3·7	34·5
78	342	12·5	77·5	34	84·7	3·7	33·5
77	329·5	12·5	76·5	33	81·0	3·0	32·5
76	317	11·5	75·5	32	78·0	2·7	31·5
75	305·5	10·5	74·5	31	75·3	2·6	30·5
74	295	8	73·5	30	72·7	3·0	29·5
73	287	10	72·5	29	70·7	3·2	28·5
72	277	9·25	71	28	67·5	1·8	27·5
70	258·5	9	69	27	65·7	1·9	26·5
68	240·5	7·25	66	26	63·8	2·0	25·5
66	226	6·5	65	25	61·8	2·3	24·5
64	213	5·75	63	24	59·5	2·0	23·5
62	201·5	5·25	61	23	57·5	2·0	22·5
60	191	5·5	59·5	22	55·5	2·5	21·5
59	185·5	5·0	58·5	21	53·0	2·0	20·5
58	180·5	5·2	57·5	20	51·0	2·6	19·5
57	175·3	5·0	56·5	19	48·4	+0·84	19 to 9
56	170·3	4·8	55·5	9	36·0	−1·67	9 to 6
55	165·5			6	41·0		

TABLE XIX.—*Heat evolved on mixing Sulphuric Acid Solutions with Water. Differentiation of the Smoothed Curve representing the Results.*

First differentiation.				Second differentiation.			
p.	D.	$\frac{dD}{dp}$.	*p*.	*p*.	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	*p*.
9	329·7	40·4	8·5	9	40·83	·91	8·5
8	289·3	39·4	7·5	8	39·92	1·05	7·5
7	249·9	38·1	6·5	7	38·87	1·24	6·5
6	211·8	36·9	5·5	6	37·63	1·48	5·5
5	174·9	35·4	4·5	5	36·15	1·65	4·5
4	139·5	43·3	3·8	4	34·50	—	—
3·6	122·20	35·8	3·5	3·6	35·7	−2·0	3·5
3·4	115·05	36·0	3·3	3·4	36·1	−1·75	3·3
3·2	107·85	37·0	3·1	3·2	36·45	−1·25	3·1
3	100·45	36·3	2·9	3·0	36·7	− ·75	2·9
2·8	93·20	37·0	2·7	2·8	36·85	− ·50	2·7
2·6	85·83	36·7	2·5	2·6	36·95	+ ·25	2·5
2·4	78·50	36·8	2·3	2·4	36·9	1	2·3
2·2	71·15	35·8	2·1	2·2	36·7	1·50	2·1
2	64·00	36·3	1·9	2	36·4	1·75	1·9
1·8	56·75	35·4	1·7	1·8	36·05	2	1·7
1·6	49·67	35·6	1·5	1·6	35·56	2·75	1·5
1·4	42·55	34·9	1·3	1·4	35·10	2·75	1·3
1·2	35·57	34·4	1·15	1·2	34·55	−15·50	1·15
1·1	32·13	35·8	1·05	1·1	36	+ 5·7	1·05
1	28·55	35·1	·95	1	35·43	7·3	·95
·9	25·04	34·1	·85	·9	34·7	9	·85
·8	21·63	33·1	·75	·8	33·8	10·5	·75
·7	18·32	32·3	·65	·7	32·75	12	·65
·6	15·09	30·8	·55	·6	31·55	13·5	·55
·5	12·01	29·6	·475	·5	30·2	15	·45
·45	10·53	29·0	·425	·4	28·7		
·40	9·08						
	From D/*p* curve.						
1·2	35·72	33·5	1·15	1·2	33·10	− 8·2	1·15
1·1	32·37	34·4	1·05	1·1	33·92	− 3·5	1·05
1	28·93	34·0	·95	1	34·27	− 1·3	·95
·9	25·53	34·9	·85	·9	34·40	+ 2·7	·85
·8	22·04	34·0	·75	·8	34·13	5·6	·75
·7	18·64	33·4	·65	·7	33·57	9·5	·65
·6	15·30	31·6	·55	·6	32·62	12·7	·55
·5	12·14	31·2	·475	·5	31·35	16·3	·455
·45	10·38	33·4	·425	·4	29·72	+50·4	·375
·40	8·91	25·6	·375	·35	27·20	−12·6	·325
·35	7·63	28·1	·325	·3	27·83	+ 4·6	·275
·30	6·225	27·74	·275	·25	27·60	18·6	·225
·25	4·838	27·68	225	·20	26·67	33·8	·175
·20	3·454	25·88	·175	·15	24·94	47·6	·12
·15	2·160	24·60	·125	·10	22·60 20·40	26·0	·09
·10	·930	18·50	·09	·08	15·20		
·08	·560						

TABLE XIX—*continued.*

First differentiation.				Second differentiation.			
p.	D.	$\frac{dD}{dp}$.	*p*.	*p*.	$\frac{dD}{dp}$.	$\frac{d^2D}{dp^2}$.	*p*.
·08	·560			·08	15·20		
		12·79	·07			22·8	·07
·06	·3042			·06	10·75		
		3·65	·05			198	·05
·04	·1312			·04	6·8		
		5	·03			178	·03
·02	·0312			·02	+ 3·25		
		1·56	·01			170	·01
0	0			0	− ·15		
Another reading.							
·16	2·48			·016	+35·0		
		32·0	·15			287·5	·15
·14	1·84			·14	29·25		
		26·8	·13			270·0	·13
·12	1·304			·12	23·85		
		23·7	·11			242·5	·11
·10	·89			·10	19·0		
		16·7	·09			217·5	·09
·08	·556			·08	14·65		
		12·8	·07			207·5	·07
·06	·30			·06	10·55		
		8·6	·05			185	·05
·05	·128			·04	6·8		
		4·9	·03			175	·03
·02	·030			·02	3·3		
		1·5	·01			160	·01
0	0			0	·1		

TABLE XX.—*Decrease of Density of Sulphuric Acid Solutions by Heat. Unreduced Values.*

p.	From 28·06° to 38·20°.	From 7·99° to 28·06°.	From 7·99° to 38·20°.	*p*.	From 28·06° to 38·20°.	From 7·99° to 28·06°.	From 7·99° to 38·20°.
99·93	·009948	·020314	·030262	69·98	·008925	·018392	·027317
98·85	·009664	·020292	·029956	68·06	·008770	·018084	·026863
97·60	·009810	·020255	·030065	66·06	·008648	·017851	·026497
96·82	·009793	·020338	·030131	64·09	·008524	·017535	·026059
95·95	·009893	·020364	·030237	61·95	·008115	·017311	·025426
95·08	·009952	·020474	·030426	60·01	·008155	·016959	·025114
93·97	·010051	·020745	·030796	57·90	·008078	·016587	·024665
93·06	·010160	·020804	·030964	56·05	·007996	·016416	·024412
91·93	·010284	·021059	·031343	54·04	·007868	·016154	·024022
91·09	·010384	·021249	·031631	52·07	·007800	·015969	·023759
89·92	·010489	·021519	·032008	50·11	·007727	·015743	·023470
89·09	·010557	·021755	·032312	48·07	·007642	·015553	·023195
87·91	·010690	·021936	·032626	45·76	·007549	·015366	·022915
87·09	·010709	·022117	·032824	43·53	·007500	·015421	·022741
85·92	·010737	·022113	·032850	41·81	·007471	·015113	·022584
85·04	·010676	·022040	·032716	39·68	·007586	·014999	·022385
84·08	·010639	·021904	·032543	37·76	·007331	·014880	·022211
83·04	·010433	·021780	·032213	35·74	·007263	·014734	·021997
81·91	·010379	·021280	·031659	33·87	·007172	·014553	·021725
81·15	·010134	·020946	·031080	31·83	·007016	·014346	·021361
80·03	·010065	·020652	·030717	29·80	·007010	·014037	·021047
79·04	·009894	·020305	·030199	27·77	·006817	·013739	·020556
78·00	·009747	·019974	·029721	26·18	·006691	·013394	·020085
75·96	·009484	·019486	·028970	23·85	·006481	·012853	·019334
74·04	·009315	·019070	·028385	21·94	·006291	·012347	·018638
72·07	·009104	·018697	·027801	19·86	·006074	·011783	·017857

TABLE XXI.—*Decrease of Density, and Expansion, of Sulphuric Acid Solutions by Heat.*

Reduced Values.

All the Values, except those for p, being multiplied by 10^6.

p.	28–38°.		18–28°.		8–18°.		18–38°.	8–28°.	8–38°, Diff. of Dens. (E).		
	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	*d*E.	*p*.
100	5448	9883	5450	9940	5638	10343	19823	20283	30166	—	—
99·8	—	—	—	—	—	10327	—	—	—	—	—
99·6	—	—	—	—	—	10327	—	—	—	+82	99·5
99·4	—	—	—	—	—	10313	—	—	—	—	—
99·2	—	—	—	—	—	10291	—	—	—	—	—
99	5437	9881	5431	9924	5594	10279	19805	20203	30084	—	—
98·8	—	—	—	—	—	10267	—	—	—	—	—
98·6	—	—	—	—	—	10256	—	—	—	+157	98·5
98·4	—	—	—	—	—	10256	—	—	—	—	—
98·2	—	—	—	—	—	10260	—	—	—	—	—
98	5810	9658	5460	9985	5593	10284	19643	20269	29927		
97·5	—	—	—	—	—	10247	—	—	—	+36	97·5
97	5335	9704	5441	9950	5568	10237	19654	20187	29891	—	—
96·5	—	—	—	—	—	10227	—	—	—	−132	96·5
96	5365	9752	5463	10026	5598	10245	19778	20271	30023	−163	95·5
95	5408	9820	5522	10080	5603	10286	19900	20366	30186	−214	94·5
94	5467	9911	5542	10102	5667	10387	20013	20489	30400	−342	93·5
93	5583	10018	5537	10203	5751	10521	20221	20724	30742	−319	92·5
92	5597	10102	5694	10336	5820	10623	20438	20959	31061	−374	91·5
91	5688	10238	5802	10503	5873	10694	20741	21197	31435	−319	90·5
90	5762	10341	5907	10661	5922	10752	21002	21413	31754	−365	89·5
89	5831	10427	5961	10723	6062	10969	21150	21692	32119	−312	88·5
88	5909	10525	6061	10863	6090	11043	21388	21906	32431	−174	87·5
87	5957	10568	6130	10940	6180	11097	21507	22037	23605	−13	86·5
86	5995	10588	6185	10989	6177	11041	21577	22030	32618	+114	85·5
85	5994	10535	6177	10929	6196	11014	21464	21943	32478	186	84·5
84	5966	10434	6154	10823	6236	11035	21257	21858	32292	323	83·5
83	5923	10297	6145	10747	6208	10925	21044	21672	31969	497	62·5
82	5890	10182	6068	10550	6139	10740	20732	21290	31472	369	81·5
81	5859	10066	6022	10407	6057	10530	20473	20937	31003	517	80·5
80	5848	9932	5916	10194	5997	10360	20126	20554	30486	521	79·5
79	5771	9790	5854	9988	5936	10187	19778	20175	29965	462	78·5
78	5727	9647	5800	9834	5880	10022	19481	19856	29503	399	77·5
77	5702	9544	5760	9678	5837	9882	19222	19569	29104	337	76·5
76	5630	9358	5732	9582	5846	9827	18940	19409	28767	330	75·5
75	5585	9220	5711	9481	5832	9736	18701	19217	28437	265	74·5
74	5605	9187	5693	9385	5792	9600	18572	18985	28172	337	73·5
73	5566	9059	5695	9321	5742	9455	18380	18776	27835	246	72·5
72	5559	8984	5674	9221	5742	9384	18205	18605	27589	228	71·5
71	5537	8884	5658	9129	5761	9348	18013	18477	27361	236	70·5
70	5528	8807	5655	9059	5748	9259	17866	18318	27125	220	69·5
69	5526	8740	5653	8990	5737	9175	17730	18165	26905	231	68·5
68	5520	8666	5633	8893	5741	9115	17559	18008	26674	211	67·5
67	5518	8598	5636	8833	5730	9082	17431	17865	26463	226	66·5
66	5507	8523	5639	8774	5713	8940	17297	17714	26237	241	65·5
65	5484	8426	5634	8703	5702	8857	17129	17560	25986	241	64·5
64	5469	8341	5634	8641	5682	8763	16982	17404	25745	230	63·5
63	5451	8255	5658	8613	5648	8647	16868	17260	25515	218	62·5
62	5424	8153	5691	8602	5620	8542	16755	17150	25297	190	61·5
61	5430	8105	5715	8576	5584	8426	16681	17002	25107	218	60·5
60	5437	8056	5703	8495	5566	8338	16551	16833	24889	174	59·5
59	5462	8034	5700	8429	5548	8252	16463	16681	24715	211	58·5
58	5458	7971	5702	8372	5526	8161	16343	16533	24504	86	57·5
57	5446	7930	5719	8337	5559	8151	16267	16488	24418	199	56·5
56	5474	7881	5707	8261	5548	8077	16142	16338	24219	186	55·2
55	5467	7814	5707	8202	5546	8017	16016	16219	24033	189	54·5
54	5477	7774	5688	8117	5541	7953	15891	16070	23844	115	53·5
53	5474	7715	5666	8019	5603	7985	15744	16004	23729	131	52·5
52	5492	7686	5650	7950	5611	7944	15686	15894	23580	133	51·5
51	5513	7661	5665	7916	5601	7870	15577	15786	23447	159	50·5
50	5523	7622	5657	7850	5602	7816	15472	15666	23288	149	49·5
49	5522	7568	5653	7792	5615	7779	15360	15571	23139		

TABLE XXI—*continued.*

p.	28—38°.		18—28°.		8—18°.		18—38°.	8—28°.	8—38°, Diff. of Dens. (E).		
	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Expn.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	Diff. of Dens.	*d*E.	*p*.
49	5522	7568	5653	7792	5615	7779	15360	15571	23139	122	48·5
48	5536	7535	5665	7738	5626	7744	15273	15482	23017	119	47·5
47	5540	7488	5670	7707	5635	7703	15195	15410	22898	105	46·5
46	5558	7461	5687	7677	5639	7655	15138	15332	22793	100	45·5
45	5566	7417	5682	7621	5670	7655	15038	15276	22693	84	44·5
44	5596	7410	5678	7567	5699	7632	14977	15199	22609	96	43·5
43	5611	7380	5722	7568	5687	7565	14948	15133	22513	91	42·5
42	5640	7363	5731	7533	5695	7526	14896	15059	22422	84	41·5
41	5662	7347	5740	7489	5726	7512	14836	15001	22348	98	40·5
40	5663	7298	5753	7457	5750	7495	14755	14952	22250	90	39·5
39	5670	7258	5784	7442	5757	7455	14705	14902	22160	85	38·5
38	5696	7243	5785	7398	5777	7434	14641	14882	22075	107	37·5
37	5704	7204	5803	7372	5786	7392	14576	14764	21968	118	36·5
36	5709	7159	5788	7307	5818	7384	14466	14691	21850	127	35·5
35	5727	7138	5797	7266	5805	7319	14404	14585	21723	136	34·5
34	5729	7093	5807	7230	5804	7264	14323	14494	21587	147	33·5
33	5728	7044	5795	7168	5810	7228	14212	14396	21440	138	32·5
32	5725	6993	5790	7114	5813	7195	14107	14319	21302	188	31·5
31	5721	6943	5759	7027	5820	7144	13970	14171	21114	185	30·5
30	5730	6917	5733	6950	5800	7072	13857	14022	20929	223	29·5
29	5716	6844	5718	6886	5760	6976	13730	13862	20706	234	28·5
28	5670	6745	5704	6824	5738	6903	13569	13727	20472	287	27·5
27	5633	6657	5657	6722	5695	6806	13379	13528	20185	301	26·5
26	5610	6585	5595	6605	5639	6694	13190	13299	19884	323	25.5
25	5565	6490	5545	6502	5571	6569	12992	13069	19561	336	24·5
24	5537	6414	5465	6366	5503	6445	12780	12811	19225	340	23·5
23	5490	6319	5416	6267	5414	6299	12586	12566	18885	351	22·5
22	5445	6224	5341	6141	5339	6169	12365	12310	18534	370	21·5
21	5385	6116	5274	6022	5249	6026	12138	12048	18164	357	20·5
20	5324	6007	5227	5929	5149	5871	11936	11800	17807		

TABLE XXI—*continued.—Decrease of Densities of Sulphuric Acid Solutions between 8 and 18°.*

p.	Expn.	Diff. of Dens.	p.	Expn.	Diff. of Dens.	p.	Expn.	Diff. of Dens.
19	5025	5692	7	2777	3152	1·8	—	1773
18	4892	5504	6	2526	2885	1·6	—	1704
17	4769	5329	5	2281	2607	1·4	—	1646
16	4632	5162	4·5	—	2467	1·2	—	1599
15	4482	4937	4·0	2057	2339	1·0	1529	1538
14	4312	4756	3·5	—	2231	0·8	—	1469
13	4180	4549	3·0	1806	2096	0·6	—	1403
12	3975	4297	2·8	—	2049	0·4	—	1350
11	3807	4088	2·6	—	1998	0·3	—	1339
10	3432	3878	2·4	—	1928	0·2	—	1286
9	3240	3636	2·2	—	1870	0·1	—	1232
8	3014	3413	2·0	—	1828	0	1194	1195

TABLE XXII.—*Decrease of Densities of Sulphuric Acid Solutions by Heat. Differentiation of the Smoothed Curve representing the Results between 8° and 38°.*

First differentiation.				Second differentiation.			
p.	E 10^6.	$\frac{dE}{dp} 10^6$.	*p*.	*p*.	$\frac{dE}{dp} 10^6$.	$\frac{d^2E}{dp} 10^6$.	*p*.
100	30170	120	99·75	100	127	20	99·75
99·5	30110	120	99·25	99·5	117	24	99·25
99	30050	120	98·75	99	105	24	98·75
98·5	29990	80	98·25	98·5	93	34	98·25
98	29950	70	97·75	98	76	38	97·75
97·5	29915	50	97·25	97·5	57	304	97·25
97	29890	−110	96·75	97	− 95	44	96·75
96·5	29945	−140	96·25	96·5	−117	50	96·25
96	30015	−140	95·75	96	−142	52	95·75
95·5	30085	−200	95·25	95·5	−168	48	95·25
95	30185	−200	94·75	95	−192	60	94·75
94·5	30285	−230	94·25	94·5	−222	56	94·25
94	30400	−270	93·75	94	−250	54	93·75
93·5	30535	−380	93·25	93·5	−277	56	93·25
93	30725	−330	92·75	93	−215	60	92·75
92·5	30890	−340	92·25	92·5	−345	20	92·25
92	31060	−350	91·75	92	−355	4	91·75
91·5	31235	−360	91·25	91·5	−357	4	91·25
91	31415	−360	90·75	91	−359	2	90·75
90·5	31595	−360	90·25	90·5	−360	4	90·25
90	31775	−370	89·75	90	−362	− 4	89·75
89·5	31960	−360	89·25	89·5	−360	− 6	89·25
89	32140	−320	88·75	89	−357	− 60	88·5
88·5	32300	−270	88·25	88	−227	−127	88 to 84
88	32435	−200	87·75	84	+280	—	—
87·5	32535	−110	87·25	83·5	503	+ 2	83·5 to 78·5
87	32590	− 60	86·75	78·5	492	—	—
86·5	32620	0	86·25	77 5	365	21	77·5 to 73·5
86	32620	+ 70	85·75	73·5	280	—	—
85·5	32585	110	85·25	72·5	235	5	72·5 to 63·5
85	32530	190	84·75	63·5	230	—	—
84·5	32435	240	84·25	62·5	195	4	62·5 to 50
84	32315	330	83·75	50	142	12	49·5
83·5	32145	350	83·25	49	130	6	48·5
83	31975	505	82·5	48	124	9	47·5
82	31470	490	81·5	47	115	12	46·5
81	30980	510	80·5	46	103	8	45·5
80	30470	500	79·5	45	95	3	44·5
79	29970	490	78·5	44	92	2	43·5
78	29480	370	77·5	43	90	3	42·5
77	29110	350	76·5	42	87	0	41·5
76	28760	325	75·5	41	87	2	40·5
75	28435	295	74·5	40	85	+ 5	39·5
74	28130	290	73·5	39	80	− 27	38·5
73	27840	240	72·5	38	107	− 3	37·5
72	27600	240	71·5	37	110	− 12	36·5
71	27360			36	122		

TABLE XXII—*continued.*

First differentiation.				Second differentiation.			
p.	E 10^6.	$\frac{dE}{dp}10^6$.	*p*.	*p*.	$\frac{dE}{dp}10^6$.	$\frac{d^2E}{dp}10^6$.	*p*.
71	27360	225	70·5	36	122	− 11	35·5
70	27315	245	69·5	35	133	− 7	34·5
69	27890	225	68·5	34	140	− 7	33·5
68	27665	220	67·5	33	147	− 13	32·5
67	27445	235	66·5	32	160	− 13	31·5
66	27210	235	65·5	31	173	− 13	30·5
65	26975	230	64·5	30	180	− 15	29·5
64	26745	240	63·5	29	195	− 80	28·5
63	26505	215	62·5	28	275	− 18	27·5
62	26290	195	61·5	27	293	− 18	26·5
61	26095	180	60·5	26	315	− 12	25·5
60	25915	195	59·5	25	327	− 13	24·5
59	25720	160	58·5	24	340	− 8	23·5
58	25560	180	57·5	23	348	− 4	22·5
57	25380	165	56·5	22	352	− 5	21·5
56	25215	175	55·5	21	357	− 5	20·5
55	25040	165	54·5	20	362		
54	24875	155	53·5				
53	24720	150	52·5				
52	24570						

First differentiation continued.

p.	E 10^6.	$\frac{dE}{dp}10^6$.	*p*.	*p*.	E 10^6.	$\frac{dE}{dp}10^6$.	*p*.
52	24570	165	51·5	36	22850	125	35·5
51	24415	135	50·5	35	22725	135	34·5
50	24280	140	49·5	34	22590	145	33·5
49	24140	140	48·5	33	22445	160	32·5
48	24000	110	47·5	32	22285	180	31·5
47	23890	105	46·5	31	22105	180	30·5
46	23785	100	45·5	30	21925	190	29·5
45	23685	95	44·5	29	21735	265	28·5
44	23590	95	43·5	28	21470	280	27·5
43	23495	80	42·5	27	21190	310	26·5
42	23415	90	41·5	26	20880	315	25·5
41	23325	85	40·5	25	20565	320	24·5
40	23240	80	39·5	24	20245	355	23·5
39	23160	80	38·5	23	19890	355	22·5
38	23080	110	37·5	22	19535	365	21·5
37	22970	120	36·5	21	19170	365	20·5
36	22850			20	18805		

TABLE XXII—*continued.*

First differentiation, between 8° and 18°.

p.	E 10^6.	$\frac{dE}{dp}10^6$.	*p.*
100	10350		
		90	99·75
99·5	10305		
		60	99·25
99·0	10275		
		50	98·75
98·5	10250		
		20	98·25
98·0	10240		
		0	97·75
97·5	10240		
		30	97·25
97·0	10225		
		0	96·75
96·5	10225		
		− 16	96·25
96·0	10233		
		− 48	95·75
95·5	10257		
		− 6	95·25
95·0	10290		
		− 80	94·75
94·5	10330		
		−120	94·25
94·0	10390		
29	6980		
		80	28·5
28	6900		
		100	27·5
27	6800		
		105	26·5
26	6695		
		120	25·5
25	6575		
		120	24·5
24	6455		
		140	23·5
23	6315		
		140	22·5
22	6175		
		145	21·5
21	6030		
		160	20·5
20	5870		

p.	E 10^6.	$\frac{dE}{dp}10^6$.	*p.*
20	5870		
		170	19·5
19	5700		
		185	18·5
18	5515		
		185	17·5
17	5330		
		185	16·5
16	5145		
		205	15·5
15	4940		
		200	14·5
14	4740		
		210	13·5
13	4530		
		215	12·5
12	4315		
		220	11·5
11	4095		
		220	10·5
10	3875		
		235	9·5
9	3640		
		250	8·5
8	3390		
		245	7·5
7	3145		
		270	6·5
6	2875		
		265	5·5
5	2610		
		280	4·5
4	2330		
		220	3·75
3·5	2220		
		140	3·25
3·0	2100		
		260	2·75
2·5	1970		
		280	2·25
2·0	1830		
		290	1·75
1·5	1685		
		200	1·25
1·0	1535		
		220	0·75
0·5	1375		

Second differentiation, between 8° and 18°.

p.	$\frac{dE}{dp}10^6$.	$\frac{d^2E}{dp^2}10^6$.	*p.*
99·75	90		
		+ 43	99·75 to 97·75
97·75	5		
		− 22	97·5
97·25	27		
		+ 42	97·25 to 94·25
94·25	−100		
28	92		
		− 8	28 to 19
19	180		

p.	$\frac{dE}{dp}10^6$.	$\frac{d^2E}{dp^2}10^6$.	*p.*
19	180		
		− 4	19 to 10·5
10·5	217		
9·5	240		
		− 5	25 to 4·5
4·5	277		
4·0	210		
		−36	4 to 1
1·0	317		

TABLE XXIII.—*Weights of Sulphuric Acid Solutions contained in a 25 c.c. Density Bottle at t°.*

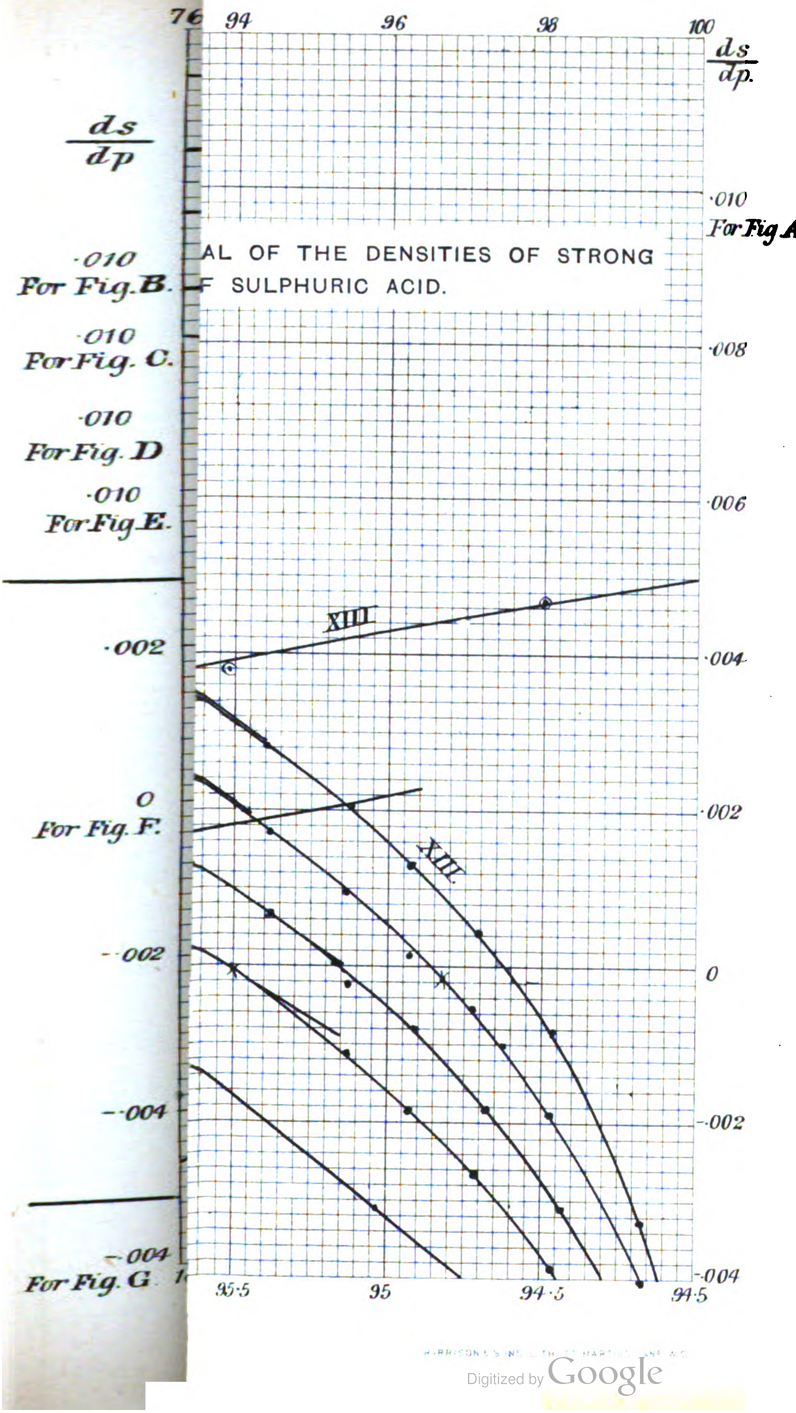
t°.	84·1970 per cent.		81·09315 per cent.		41·76736 per cent.		t°.
	w.	*dw/dt.*	*w.*	*dw/dt.*	*w.*	*dw/dt.*	
38·203	(43·80801)		(43·0737)		(32·6733)		
		(− ·0242)		(− ·0230)		(− ·0167)	37·15
36 103	43·8589		43·1219		32·7084		
		− ·0251		− ·0242		− ·0178	35·10
34·090	43·9095		43·1707		32·7441		
		− ·0252		− ·0243		− ·0177	33·08
32 075	43·9605		43·2199		32·7799		
		− ·0258		− ·0248		− ·0181	31·07
30·060	44·0125		43·2698		32·8163		
		(− ·0263)		(− ·0255)		(− ·0185)	29·06
28·064	(44·0649)	− ·0256	(43·3207)	− ·0246	(32·8533)	− ·0177	28·05
		(− ·0249)		(− ·0238)		(− ·0170)	27·05
26·036	44·1155		43·3689		32·8877		
		− ·0258		− ·0249		(− ·0163)	24·94
23·835	44·1723	—	43·4238	—	32·9235	− ·0175	23·97
		− ·0264		− ·0253		(− ·0189)	22·87
21·905	44·2233		43·4727		32·9601		
		− ·0256		− ·0246		− ·0176	20·89
19·881	44·2751		43·5224		32·9957		
		− ·0264		(− ·0270)		− ·0178	18·90
17·925	44·3269	—	(43·5753)	− ·0242	33·0305	—	17·91
		− ·0265		(− ·0213)		− ·0183	16·94
15·946	44·3794		43·6174		33·0667		
		− ·0253		− ·0255		− ·0182	14·94
13·939	44·4302		43·6685		33·1032		
		− ·0257		− ·0260		− ·0180	12·95
11·956	44·4809		43·7198		33·1387		
		− ·0261		− ·0249		− ·0185	10·98
9·995	44·5320		43·7687		33·1749		
		(− ·0276)		(− ·0253)		− ·0186	8·99
7·978	(44·5877)	− ·0271	(43·8198)	− ·0259	33·2125	—	8·01
		(− ·0265)		(− ·0265)		− ·0181	7·00
6·015	44·6397		43 8719		33·2479		

TABLE XXIV.—*List of the most convenient Scales used in the Working Diagrams.*

Property.	Scale.
Densities, 1st diff.,* 100 to 94 per cent. ..	·002 and 0·5 per cent. to the inch.
„ „ 100 „ 60 „ ..	·002 „ 2 „ „
„ „ 76 „ 0 „ ..	·0005 „ 4 „ „
„ „ 20 „ 0 „ ..	·0005 „ 2 „ „
„ „ 10 „ 0 „ ..	·001 „ 0·5 and 0·2 „ „
Contractions, 1st diff.	Same as for the densities.
Conductivities, 1st and 2nd diff.	·000001 and 2 per cent. to the inch.
Heat capacities and 1st diff., 12 to 0 per cent.	·01 „ ·05 „ „
„ „ 4 „ 0 „	·002 „ ·02 „ „
Heat of dissolution, 100 to 94 per cent. ..	500 „ 0·5 „ „
„ 100 „ 59 „ ..	500 „ 1 „ „
„ 70 „ 29 „ ..	200 „ 1 „ „
„ 40 „ 5 „ ..	100 „ 1 „ „
„ 9 „ 0 „ ..	20 „ 1 „ „
„ 5 „ 0 „ ..	10 „ ·2 „ „
„ 2 „ 0 „ ..	5 „ ·1 „ „
„ 0·16 „ 0 „ ..	·2 „ ·02 „ „
„ 1st diff., 100 to 40 p.ct.	100 „ 2 „ „
„ 1st diff., 47 to 5 p.ct.	50 „ 2 „ „
Expansion, main curves	·001 „ 2 „ „
„ curves for very weak and very strong solutions	·001 „ ·5 „ „

* All the differentials here mentioned are those obtained directly from the experimental values: the scales used for those obtained from readings of curves have been sufficiently indicated in the text, p. 68.

Journ. Chem. Soc. March 1890



AL OF THE DENSITIES OF STRONG
F SULPHURIC ACID.

HARRISON & SONS LITH. ST MARTIN'S LANE W.C.

PICKERING.

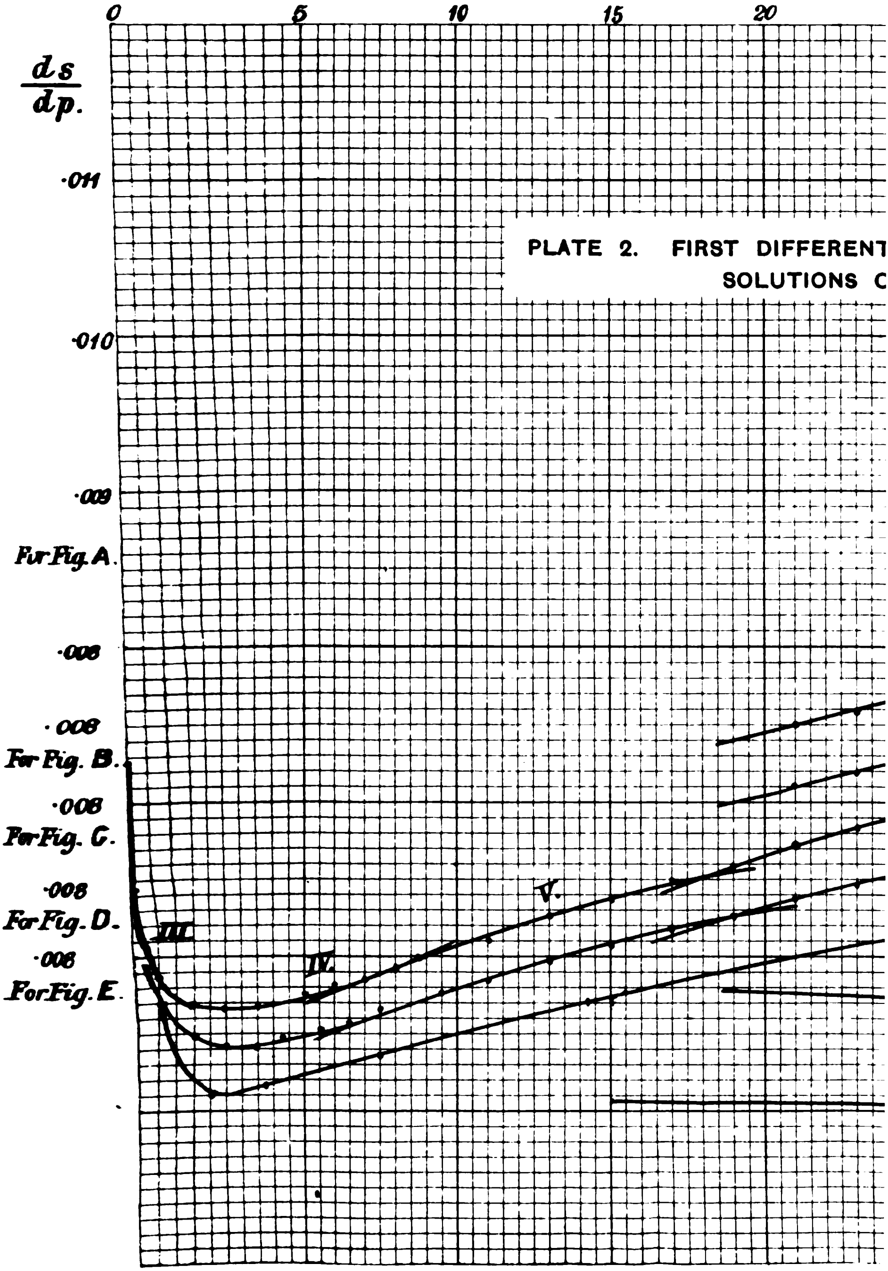
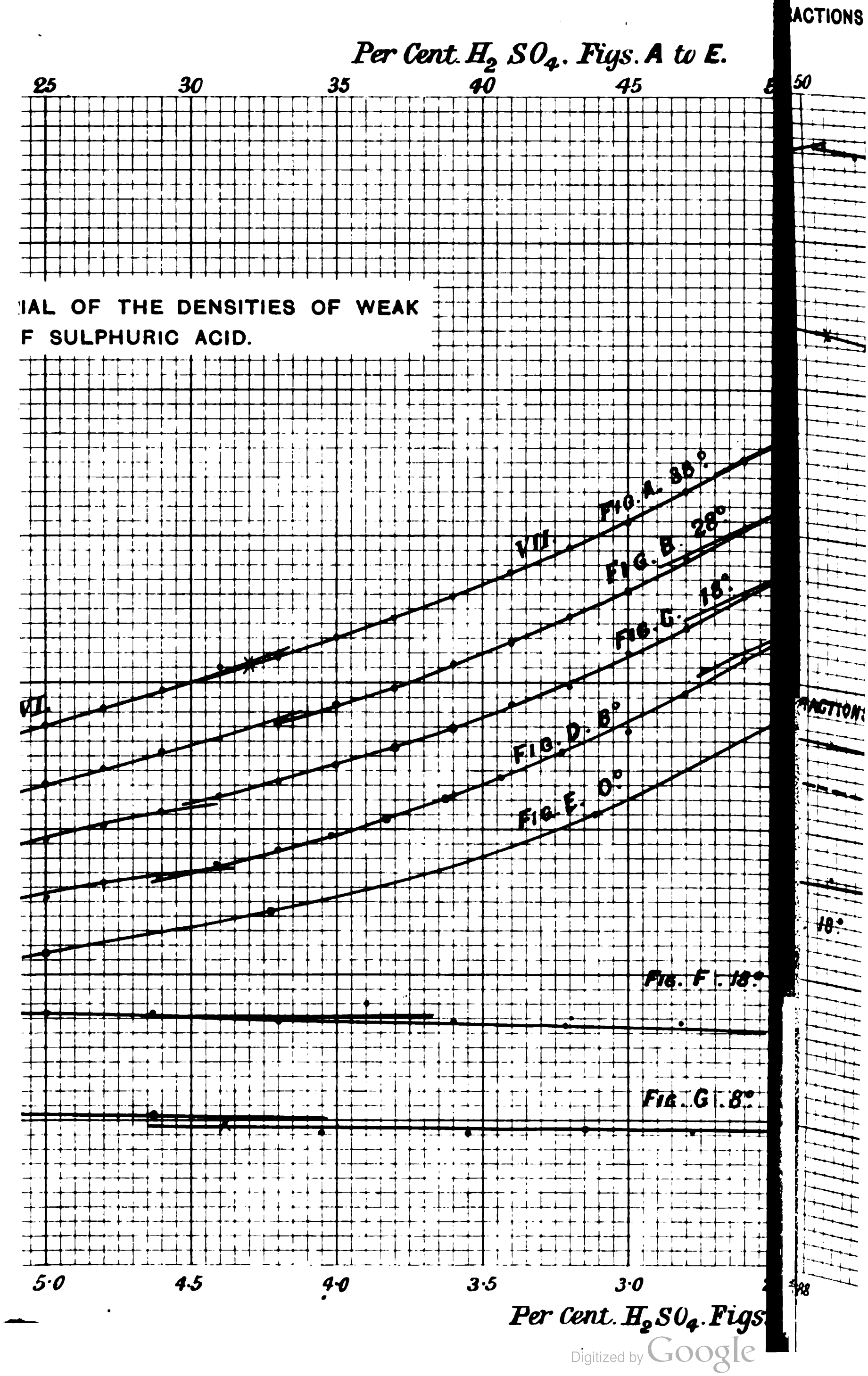
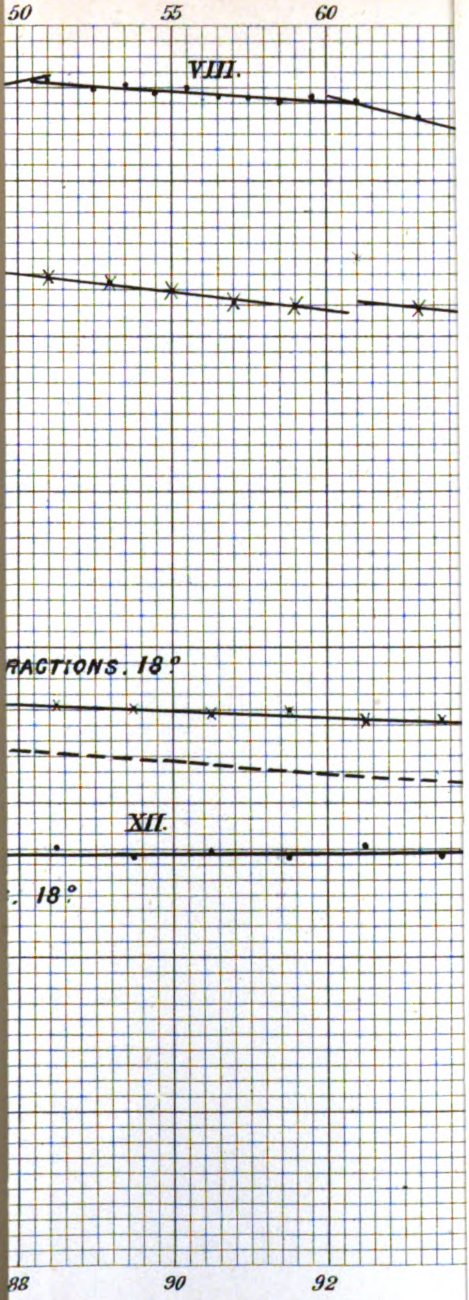


PLATE 2. FIRST DIFFERENT

SOLUTIONS C


ACTIONS
Per Cent. H_2SO_4. Figs. A to E.
25
30
35
40
45
50
IAL OF THE DENSITIES OF WEAK
F SULPHURIC ACID.
VII
VII
FIG. A. 38°
FIG. B. 28°
FIG. C. 18°
FIG. D. 8°
FIG. E. 0°
FIG. F. 18°
FIG. G. 8°
ACTIONS
18°
5·0
4·5
4·0
3·5
3·0
Per Cent. H_2SO_4. Figs

RACTIONS OF SULPHURIC ACID SOL



XI.—*A New Method of Estimating the Oxygen dissolved in Water.*

By JOHN C. THRESH, D.Sc., M.B., Medical Officer of Health.

SOME time ago, when comparing various processes for estimating nitrites in water, I was struck by the large amount of iodine which a very minute quantity of a nitrite caused to be liberated when iodide of potassium and dilute sulphuric acid are added to the water containing it. When the acid and iodide are added to such a water, the amount of iodine liberated varies with the length of time during which the mixture is exposed to the air. If air be carefully excluded, there is no increase in the amount of iodine set free after the first few minutes, and if the water be previously boiled, and allowed to cool in an atmosphere of hydrogen or coal gas, still less iodine is liberated.

In this last case the action of the acids freed by the H_2SO_4 is represented by the equation—

$$2HI + 2HNO_2 = I_2 + 2H_2O + 2NO.$$

When oxygen has access to the solution, the nitric oxide acts as a carrier, and more hydrogen iodide is decomposed, the nitric oxide apparently remaining unaffected, and capable of causing the decomposition of an unlimited quantity of the iodide.

This reaction is the one utilised in the process I have devised for estimating the oxygen dissolved in water. As 16 parts by weight of oxygen will liberate 254 parts of iodine,

$$2HI + O = H_2O + I_2,$$

and the latter element admits of being accurately estimated theoretically, the oxygen should be capable of very precise determination. Practically I find such is the case; the oxygen dissolved in drinking waters admits of being estimated both rapidly and with precision. We have simply to add to a known volume of the water a definite quantity of sodium nitrite, together with excess of potassium iodide and acid, avoiding access of air, and then to determine volumetrically the amount of iodine liberated. After deducting the proportion due to the nitrite used, the remainder represents the oxygen which was dissolved in the water and in the volumetric solution used.

It would serve no useful purpose to describe the many experiments I have made to devise the simplest and best form of apparatus, the most suitable strength for the volumetric solution, and the proper proportions of acid, of sodium nitrite, and potassium iodide.

I will merely mention that an extended series of experiments have been made to determine all these points, and the details of the process which I have to describe have all been carefully worked out.

The following are the reagents required:—

(1.) Solution of sodium nitrite and potassium iodide.

Sodium nitrite....................	0·5 gram.
Potassium iodide..................	20·0 grams.
Distilled water	100 c.c.

(2.) Dilute sulphuric acid.

Pure sulphuric acid	1 part.
Distilled water	3 parts.

(3.) A clear or fresh solution of starch.

(4.) A volumetric solution of sodium thiosulphate.

Pure crystals of thiosulphate, 7·75 grams.
Distilled water to 1 litre.
1 c.c. corresponds to 0·25 milligram of oxygen.

The apparatus required is very simple, and can readily be fitted up. It consists of a wide-mouthed white glass bottle (A, Fig. 1), of about 500 c.c. capacity, closed with a caoutchouc stopper having four perforations. Through one passes the tube B, drawn out at its lower extremity to a rather fine point, and connected at the upper end, by means of a few inches of rubber tubing, with the burette, C, containing the thiosulphate. Through another opening passes the nozzle of a separatory tube, D, having a stopper and stopcock. The capacity of this tube when full to the stopper must be accurately determined. Through the third opening passes a tube E, which can be attached to the ordinary gas supply. Through the last aperture is passed another tube, for the gas exit, and to this is attached a sufficient length of rubber tubing to enable the cork G at its end to be placed in the neck of the tube D when the stopper is removed. A small piece of glass tube projects through the cork, to allow of the escaping gas being ignited.

The apparatus is used in the following manner:—The bottle A being cleaned and dry, the perforated bung is inserted, the burette charged, and the tube B fixed in its place. E is connected with the gas supply. The tube D is filled to the level of the stopper with the water to be examined, 1 c.c. of the solution of sodium nitrite and potassium iodide added from a 1 c.c. pipette, then 1 c.c. of the dilute acid, and the stopper instantly fixed in its place, displacing a little of the water, and including no air. If the pipette be held in a vertical position with its tip just under the surface of the water, both the saline solution and the acid, being much denser than the water, flow in a sharply defined column to the lower part of the tube, so that an infinitesimally small quantity (if any) is lost in the water which overflows when the stopper is inserted. The tube is next turned upside down for a few seconds for uniform admixture to take place, and then the nozzle is pushed through the bung of the bottle, and the whole allowed to remain at rest for 15 minutes, to enable the reaction to become complete. A rapid current of coal gas is now passed through the bottle A, until all the air is displaced and the gas burns at G with a full luminous flame; the flame is now extinguished, the stopper of D removed, and the cork G rapidly inserted. On turning the stopcock, the water flows into the bottle A. The stopcock is turned off, the cork G removed, and the supply of gas regulated so that a small flame only is produced when this gas is ignited at G. Thiosulphate is now run in slowly until the colour of the iodine is nearly discharged. A little solution of starch is then

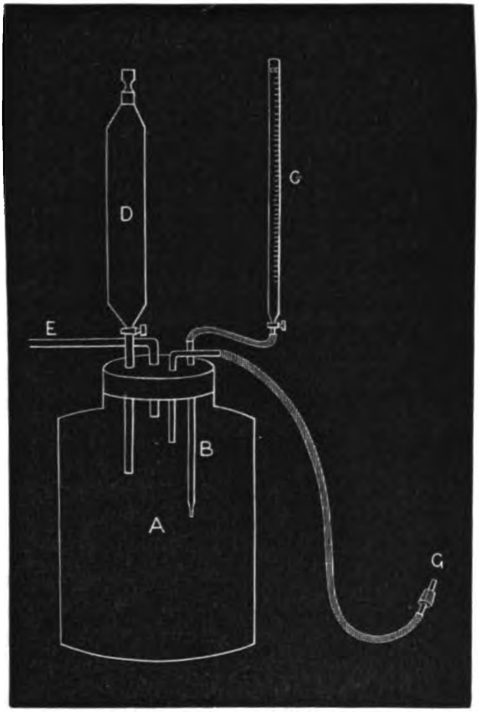


Fig. 1.—Apparatus for estimating the Oxygen dissolved in Water.

poured into D, and about 1 c.c. allowed to flow into the bottle by turning the stopcock. The titration with thiosulphate is then completed. After the discharge of the blue colour, the latter returns faintly in the course of a few seconds, due to the oxygen dissolved in the volumetric solution; after standing about two minutes, from 0·05 to 0·1 c.c. of thiosulphate must be added to effect the final discharge. The amount of volumetric solution used must now be noted. This will represent *a*, the oxygen dissolved in the water examined, + *b*, the nitrite in the 1 c.c. of solution used, and the oxygen in the acid and starch solution + *c*, a portion of the dissolved oxygen in the volumetric solution. To find the value of *a*, it is obvious that *b* and *c* must be ascertained. This can be effected in many ways, and once known does not require redetermination unless the conditions are changed.

To Find the Value of b.—Probably the best plan is to complete a determination as above described, and then, by means of the stoppered tube, introduce into the bottle in succession 5 c.c. of nitrite solution, dilute acid, and starch solution. After standing a few minutes, titrate. One-fifth of the thiosulphate used will be the value required.

To Find the Value of c.—This correction is a comparatively small one and admits of determination with sufficient accuracy if we assume that the thiosulphate solution normally contains as much dissolved oxygen as distilled water saturated at the same temperature. Complete a determination as above described, then remove the stoppered tube, and insert a tube similar to that attached to the burette, and drop in from it 10 or 20 c.c. of saturated distilled water exactly as the thiosulphate is dropped in. Allow to stand a few minutes and titrate. One-tenth or one-twentieth of the volumetric solution used, according to the number of c.c. of water added, will represent the correction for each c.c. of volumetric solution used. Call this value *d*.

Let *e* be the number of c.c. of thiosulphate used in an actual determination of the amount of oxygen in a sample of water.

f = the capacity in c.c. of the tube employed − 2 c.c., the volume of reagents added.

g = the amount of oxygen in milligrams dissolved in 1 litre of the water;

then
$$g = \frac{1000}{4f}(e - b - ed).$$

With a tube made to hold exactly 250 c.c., the most convenient quantity to use $\frac{1000}{4f}$ becomes unity, and

$$g = e - b - ed.$$

In my experiments I have used two nitrite solutions; in the first $b = 2·1$ c.c., in the second 3·1 c.c. I made a number of determinations of d at temperatures varying from 40° to 60° F., the temperature extremes in my laboratory during the past two months, and found the value of d to vary between 0·03 and 0·0315. In all my recent experiments d has been taken as 0·031.

Before passing on to the results obtained by this process, one or two points are worthy of mention.

In reference to the length of time which ought to elapse between the addition of the nitrite solution and acid and the titration, it is to be observed that I have fixed this interval at 15 minutes. Five minutes is probably sufficient, and the greater the value of e, that is, the stronger the nitrite solution, the shorter the period required to complete the reaction.

When $e = 3$ c.c. the reaction seems to be complete in five minutes, but, to be on the safe side, I prefer to fix the minimum at 15 minutes. To show the effect of time, I will quote a series of experiments made one after the other with the same sample of water.

Quantity of water taken.	Time.	Thiosulphate used.	$e - b - cd$.	Milligrams O_2 per litre.	Means.
232·5	5 mins.	11·8	8·33	8·96	8·96
322·0	5 „	15·1	11·54	8·96	
232·5	15 „	12 0	8·53	9·17	9·10
322·0	15 „	15·2	11·64	9·04	
232·5	30 „	11·95	8·48	9·12	9·08
322·0	30 „	15·20	11·64	9·04	
232·5	4 hours	11·9	8·43	9·07	9·07

The use of coal-gas is recommended, and nothing has been said about passing it over alkaline pyrogallol or otherwise treating it before allowing it to pass through the apparatus. I have used it after passing through long tubes full of beads moistened with pyrogallol solution, and I have not be able to ascertain that there was the slightest advantage in so doing, providing the process is performed as I have described. I have also tried to ascertain whether there is any loss of iodine, either by chemical action of any constituent of the gas or by the mechanical action of the current. I have not been able to discover any appreciable effect.

The results obtained, however, can be made to vary, the extreme limit being less than 0·5 milligram of oxygen per litre of water, using 250 c.c. for the estimation. To quote an extreme case. In one experiment (1), after the air had been wholly expelled from the bottle A, no more gas was passed through, and the titration was effected in the closed apparatus, the volumetric solution being run in as rapidly as possible. The end reaction was not well defined. In the second experiment (2), the volumetric solution was run in very slowly drop by drop, and a brisk current of gas was kept passing through the apparatus. End reaction well defined.

	Volume of water.	Thiosulphate.	Oxygen per litre.
(1)	322 c.c.	15·35 c.c.	9·14 milligrams.
(2)	322 „	14·9 „	8·80 „

The difference is probably due to nearly all the oxygen dissolved in the thiosulphate being used up in the first case, and being lost by diffusion in the second.

In the examination of waters from various sources, and making the experiments in pairs, using tubes of different sizes, I convinced myself that exceedingly concordant results could easily be obtained.

A few of these may be quoted:—

	Source of water.	*f.* Amount of water employed.	*e.* Thiosulphate required.	$e - b - cd$.	*g.* Milligrams O per litre.
1..	Spring water....	232·5	9·5	7·11	7·64
	„	322·0	12·35	9·87	7·66
2..	Rain water	232·5	10·15	7·74	8·32
	„	322·0	13·05	10·55	8·19
3..	Shallow well water.......	232·5	8·95	6·57	7·07
		322·0	11·35	8·90	6·91
4..	Rain water.	232·5	9·9	7·49	8·05
	„	322·0	12 95	10·45	8·11
5..	Distilled water shaken with air	232·5	12 05	9·58	10·30
		322·0	16·00	13·40	10·40

As Sir Henry Roscoe and Mr. Lunt have recently determined with great care the amount of oxygen which water freshly distilled can dissolve when agitated with air until saturated, I conducted a series of experiments determining the oxygen by my process at temperatures of 10°, 15°, 20°, 25°, and 30° C. respectively.

The following are the results obtained:—

Temperature 10° *C.*

	Quantity of water taken.	Thiosulphate used.	*e* − *b* − *cd*.	Milligrams of Oxygen per litre.	Difference from mean.
1..	232·5	13 0	10·50	11·29	+0·12
2..	232·5	12·9	10·40	11·18	+0·01
3..	322·0	16·95	14·32	11·12	−0·05
4..	232·5	12·85	10·35	11·13	−0·04
5..	232·5	12·92	10·42	11·20	+0·03
6..	322·0	17·00	14·37	11·16	−0·01
7..	232·5	12·85	10·35	11·13	−0·04
			Mean....	11·17	

Barometer reading 30·05 in.
11·17 milligrams = 7·82 c.c. at N.P.T.
Roscoe and Lunt found 7·77 „ Difference +0·05 c.c.

Temperature 15° *C.*

	Quantity of water taken.	Thiosulphate used.	*e* − *b* − *cd*.	Milligrams of Oxygen per litre.	Difference from mean.
1..	322·0	15·45	12·87	9·99	−0·04
2..	322·0	15·55	12·97	10·07	+0·04
3..	232·5	11·90	9·43	10·14	+0·11
4..	232·5	11·70	9·23	9·92	−0·11
			Mean...	10·03	

Barometer reading 30 in.
10·03 milligrams = 7·02 c.c. at N.P.T.
Roscoe and Lunt found 6·96 „ Difference +0·06.

Temperature, 20° *C.*

	Water employed.	Thiosulphate used.	*e* − *b* − *cd*.	Milligrams of oxygen per litre.	Difference from mean.
1..	322·0 cc.	14·9	11·34	8·80	−0·02
2..	232·5 „	11·55	8·09	8·70	−0·12
3..	322·0 „	15·0	11·44	8·88	+0·06
4..	232·5 „	11·65	8·19	8·81	−0·01
5..	322·0 „	15·1	11·53	8·95	+0·13
6..	322·0 „	14·9	11·34	8·80	−0·02
			Mean...	8·82	

Mean barometer reading 30·05.
8·82 milligrams = 6·17 c.c. at N.P.T.
Roscoe and Lunt found 6·22 „ Difference, −0·05.

Temperature, 25° *C.*

Series 1.

	Water taken.	Thiosulphate used.	*e* − *b* − *cd*.	Milligrams of oxygen per litre.	Difference from mean.
1..	232·5	11·2	7·77	8·35	−0·015
2..	322·0	14·3	10·76	8·38	+0·015
	Barom., 30·15.		Mean....	8·365	
			Series 2.		
1..	232·5	10·75	7·32	7·88	−0·085
2..	322·0	13·9	10·37	8·05	+0·085
3..	232·5	10·8	7·36	7·91	−0·055
4..	232·5	10·9	7·46	8·02	+0·055
			Mean...	7·965	

Barometer reading, 30·1 in.

The cause of the different results obtained in Series 1 and 2, at this temperature and also at the temperature next to be considered will be referred to shortly.

Mean of the 2 series 8·165.
8·165 milligrams = 5·72 c.c. at N.P.T.
Roscoe and Lunt found 5·60 c.c. at N.P.T. Difference + 0·12.

Temperature 30° *C.*

Series 1.

	Quantity of water used.	Thiosulphate used.	*e* − *b* − *cd*.	Milligrams of oxygen per litre.	Difference from mean.
1..	232·5	11·0	7·56	8·12	+0·035
2..	322·0	13·9	10·37	8·05	−0·035
	Barom., 30·15.		Mean....	8·085	
			Series 2.		
1..	232·5	10·5	7·07	7·60	+0·02
2..	322·0	13·25	9·75	7·57	+0·01
3..	232·5	10·4	6·98	7·51	−0·05
			Mean...	7·56	

Barometer, 30·1
Mean of both series, 7·82 = 5·47 c.c. at N.P.T.
Roscoe and Lunt's calc. 5·43 „ Difference, + 0·04.

Finding in the first series of experiments that my results at 25° and 30° C. were higher than those obtained by Roscoe and Lunt, whilst at the lower temperatures they were almost identical, it struck me that the difference was probably due to the mode of saturation. The agitation in a couple of Winchesters was done as directed by them, but the water used had been previously saturated at the lower temperatures, and probably was slightly super-saturated. I then made a further series of experiments (Series 2) with freshly-distilled water, which was not agitated with air until it had attained the desired temperature. The results proved that this surmise was correct. Probably some such explanation accounts for the uniformly higher results obtained by Dittmar.

In the subjoined table, the slight corrections necessary for variation in observed barometric pressure have been made, and the figures so obtained compared with Roscoe and Lunt's determinations:—

Temperature.	Found.	Roscoe and Lunt.	Difference.
10° C.	7·81	7·77	+0·04
15° C.	7·02	6·96	+0·06
20° C.	6·17	6·22	−0·05
25° C.	(1) 5·82 (2) 5·56 } 5·69	5·60	+0·09
30° C.	(1) 5·63 (2) 5·27 } 5·45	5·43	+0·02

It is obvious from the results so obtained that, at any rate in pure water, the oxygen can be determined readily and with great accuracy by this process; but now the question arises, is the process applicable for all ordinary river, spring, and well waters? I believe that it is. No doubt there will be exceptional cases in which the process cannot be used, and others in which some modification may be required. A water containing nitrites will require the amount of the nitrous acid to be determined if the utmost accuracy is required. (A water containing 1 part of HNO_2 in 1,000,000, will affect the results +0·17 milligram of oxygen per litre, 94 parts of the acid corresponding to 16 of oxygen.) Where nitrites are present in sufficient quantity to interfere, the amount may be determined by any of the ordinary processes, but I prefer the following method:—

Take 250 c.c. of the water to be examined, rendered faintly alkaline if not already so, add a few drops of strong solution of potassium iodide, and boil vigorously for a few minutes. Then transfer to the bottle A used in the oxygen determination, and allow to get quite cold in a slow current of coal gas. Then add a few drops of dilute sulphuric acid and solution of starch, and titrate with the hyposulphite. The correction to be made in the oxygen determination is thus ascertained. One or two experimental results may be quoted.

		Quantity of water.	Thiosulphate used.	Corrected.	Milligrams of oxygen per litre.
1..	Tap water..........	232·5	13·2	9·7	10·43
2	Tap water + 5 milligrams commercial sodium nitrite	232·5	15·95	9·55	10·27
3	Tap water + 10 milligrams sodium nitrite	232·5	18·6	9·48	10·19

In number 2, the thiosulphate used by 250 c.c. of the boiled water was 2·8 c.c.

In number 3, the thiosulphate used by 250 c.c of the boiled water was 5·45 c.c.

The results are fairly satisfactory, even with such large proportions of nitrite, proportions far larger than are likely to be met with in practice. With reference to this method of estimating small quantities of nitrites, I may have something to say on a future occasion.

Nitrates do not interfere, even when present in large quantities; but fresh urine, when present to the extent of 1 per cent., has a small but very appreciable effect, as the following experiments show:—

	Water used.	Thiosulphate required.	Corrected.	Milligrams of oxygen per litre.
1..	232·5..................	11·9	8·43	9·07
2	232·5 + 0·25 gram of ammonium nitrate	11·75	8·29	8·91
3	322·0 + 0·25 gram of ammonium nitrate	15·4	11·82	9·17
1..	322·0..................	15·1	11·54	9·04
2	322·0 (containing 1 per cent. of fresh urine)	14·4	10·85	8·43

Should this process work as satisfactorily in the hands of others as it has in mine, the determination of the dissolved oxygen in water, instead of being one of the most tedious and most unsatisfactory, will become one of the simplest and most accurate of processes in the domain of water analysis. The apparatus required is of the simplest description, the solutions, &c., required are already to be found in every laboratory, and the whole determination can be effected in considerably less than half an hour.

Since reading the paper, I have determined the oxygen dissolved in distilled water saturated at 1° and 5° C. respectively with the following results:—

Temperature, 1° *C.*

	Quantity of water used.	Thiosulphate required.	*e* − *b* − *ed*.	Milligrams of oxygen per litre.	Difference from mean.
1..	232·5	16·50	12·99	13·97	−0·06
2..	322·0	21·90	18·22	14·16	+0·12
3..	232·5	16·50	12·99	13·97	−0·06
				Mean 14·03	

14·03 milligrams = 9·82 c.c. at N.P.T.
Calculated from Roscoe and Lunt's table, 9·30 c.c. Difference +0·52 c.c.

Temperature, 5° *C.*

	Quantity of water taken.	Thiosulphate used.	*e* − *b* − *ed*.	Milligrams of oxygen per litre.	Difference from mean.
1..	232·5	15·3	11. 83	12·72	+0·07
2..	322·0	19·9	16·28	12·64	−0·01
3..	232·5	15·1	11·64	12·52	−0·13
4..	322·0	20·0	16·38	12·72	+0·07
				Mean 12·65	

12·65 milligrams = 8·85 c.c. at N.P.T.
Roscoe and Lunt give 8·68 „ Difference +0·17.

XII.—*The Constituents of Flax.*

By C. F. Cross and E. J. Bevan.

In the exogenous stem of the flax plant, the three types of compound celluloses are represented. In commercial flax, there is associated with the fibre proper, which is a pure pectocellulose, a certain proportion of wood and cuticular tissue, varying according to the nature of the "retting," "scutching," and other processes through which it has passed.

The present communication has reference to certain constituents of flax, which were isolated from it by solution in hot alcohol, being derived from and associated with the cuticular tissues.

In previous investigations these constituents have usually been grouped together as "alcoholic extract," "fat and wax," &c. Even Kolb, in his report on flax to the Soc. Ind. of Mulhouse (1868), has given no special account of them. The most complete investigation is that of F. Hodges, of Belfast, in a paper published in the *Proceedings of the Royal Irish Academy*, vol. 3, 460. The subject has been brought under our notice in connection with certain new processes for the treatment of flax, and we will briefly describe such of the results of our investigations as may be of interest to the Society.

The method of preparation consisted in treating a large quantity of carefully prepared Irish flax yarns with boiling alcohol. On cooling the filtered solution, a large proportion separated in the form of a pale-green magma, which melted in warm water and formed a greenish, resinous mass; this we shall refer to as A. The filtrate had a bright, chlorophyll-green colour, and on distilling off the alcohol, a brownish-green, pasty mass remained (B).

Several varieties of flax were quantitatively examined in this way with the following results:—

	Irish.	Courtrai.	Flemish.
Percentage A	1·5	2·1	2·0
„ B	2·1	1·3	1·7

The two products from the Irish flax were first examined for nitrogen and mineral matter—

	Nitrogen.	Mineral matter.	Phosphoric acid (P_2O_5). on 100 parts ash.
A........	0·09	1·7	7·0
B........	0·29	1·1	18·4

The nitrogen and phosphoric acid indicated the presence of chlorophyll, or products of its decomposition.

An elementary analysis of A gave the following numbers:—C 78·8, H 12·9; from these and from its general behaviour it was evident that we were dealing with a wax complex. It combined directly with acetic anhydride, yielding an acetate melting at 64—65°, from which we concluded that it contained free wax alcohol; the saponification numbers of the acetate showed that this was ceryl alcohol (see below).

Before proceeding further with our results we will give a short account of Hodges' investigations. By exhausting flax with ether he obtained 3·88 per cent. of an extract, and on subsequently treating with alcohol an additional 0·45 per cent.

The portion of the whole mass insoluble in cold alcohol, corresponding to our A, he analysed, and found it to contain C 79·1—79·9, H 13·2—13·5. Of nitrogen and mineral matter he makes no mention.

He then fused it with potash, and from the product there was finally obtained a wax alcohol melting at 82°, and therefore assumed to be ceryl alcohol, and a small quantity of a wax acid melting at 82° (cerotic), which was converted into an ethyl ether melting at 60—61°. Accompanying these substances there was a large proportion of ill-defined products of decomposition.

Our investigation of the portion insoluble in cold alcohol (A) was more detailed, and we find it to be a more complex mixture than would appear from the above.

On saponifying with normal alcoholic potash and converting into barium salts, we obtained 55 per cent. soluble in alcohol, and 48 per cent. insoluble and combined with barium. Accompanying the wax alcohol was an oily mixture of substances soluble in cold alcohol, the solution having an orange-green fluorescence. They are soluble in solution of sodium acetate, and are precipitated therefrom by phenylhydrazine salts in orange flocks, which become crystalline on standing. They appear to be ketones or ketols.

The wax alcohol was fractionated with ether alcohol, and the extreme fractions analysed with the following results:—

No. 1. 0·2204 gram gave 0·2830 H_2O and 0·6565 CO_2.
No. 2. 0·2200 „ 0·2765 „ 0·6565 CO_2.

	No. 1.	No. 2.	Calculated for $C_{23}H_{47}OH$.	Calculated for $C_{27}H_{55}OH$.
C......	81·1	81 3	81·2	81·8
H......	14·2	14·1	14·1	14·1

These results agree more closely with the C_{23} than the C_{27} formula, and in a preliminary note (*Chem. News*, 59, 135) we assigned the former formula to the alcohol. The results of the saponification of the acetate, however, indicate the higher molecular weight.

			Mol. wt.	Mol. wt. cal. for $C_{27}H_{55}C_2H_3O_2$.
1·000 gram	required	22·0 c.c. $\frac{N}{10}$·NaOH	455	438
1·793	"	39·1 " "		

The combustion of the acetate gave the following results:—

0·2230 gram gave 0·2672 H_2O and 0·6408 CO_2.

		Calculated for $C_{27}H_{55}C_2H_3O_2$.
C	79·1	79·4
H	13·3	13·2

The alcohol melts at 81·5—82·0°, and the acetate at 65·5°.

These results lead us to conclude, as Hodges had predicted, that the characteristic wax alcohol of flax is ceryl alcohol. Prolonged treatment (18 hours) with stronger solutions of alkalis (an alcoholic solution containing 40 grams sodium hydrate and 30 grams potassium hydrate in 1000 c.c.) showed no further resolution. But on fusing the portion unresolved by alcoholic potash with soda, precipitating the solution with barium chloride, and exhausting the dried precipitate with boiling alcohol, we obtained a further small quantity of wax alcohol melting at 86°, and two fatty acids (*a* and *b*), which were separated by taking advantage of the difference in solubility of their sodium salts in alcohol.

a. The yield of this amounted to 6 per cent. of the original product A. It melted at 82°, from which fact and from the molecular weight, 396, calculated from the amount of soda necessary to neutralise it (0·648 required 16·9 c.c. N/10 solution), we concluded it to be cerotic acid.

b. The yield of this acid was about the same. It melted at 53°, and had a molecular weight of 298 (0·745 required 25 c.c. N/10 soda).

That portion of the extract soluble in cold alcohol, which we have called B, proved to be a complicated mixture consisting chiefly of degradation-products of chlorophyll.* For the sake of comparison, we intend to investigate the alcoholic extracts of fresh grasses:* in the meantime we give a brief account of its general properties.

---

* On treatment with sodium thiosulphate (Schützenberger) in presence of alkali, the greenish-brown colour of the alkaline solution gave place to a bright chlorophyll green.

Boiling water dissolves a tarry substance which reduces Fehling's solution, and yields furfuraldehyde on hydrolysis. It forms insoluble compounds with the halogens, and soluble, yellow acid derivatives when treated with nitric acid. This portion of the extract is doubtless derived from the lignified tissue of the flax. The portion insoluble in boiling water, on saponification with alcoholic potash and treatment with barium chloride, yields a further quantity (about 10 per cent.) of ceryl alcohol, and about 15 per cent of a peculiar oil soluble in cold alcohol, the solution having an orange-green fluorescence. This "oil" proved to be a ketone: it does not reduce Fehling's solution, but it yields a bright-orange, crystalline precipitate with phenylhydrazine salts, and is resolved into a mixture of fatty acids on oxidation. It has the characteristic odour of raw flax. The portion of the barium precipitate insoluble in alcohol consists of a mixture of substances of a very indefinite character loosely combined with the barium, and which we have found it impossible to resolve satisfactorily into *proximate* constituents.

As a general summary of the results of investigations of this important group of flax constituents, we may note: (1) they are compounds for the most part of very high molecular weight; (2) "neutral" in character; (3) when proximately resolved, yield alcohols and ketones, but *no acids*, except under severe treatment involving oxidation.

We now wish to record a few observations on the constituents of the flax fibre proper. Associated with the cellulose there is about 25 per cent. of a group of pectic substances easily soluble in weak boiling alkali (1—2 per cent.), which at the same time colours them deep-yellow. They yield mucic acid on oxidation with nitric acid of sp. gr. 1·15. In one instance we obtained from 18 grams of flax as much as 0·4 gram of mucic acid, equal to a yield of 9 per cent. on the original non-cellulose constituents.

In the light of the results previously given, we have repeated the experiments described in a recent paper by R. Godeffroy (*Mitt. d. K.K. Techn. Ger. Mus.*, 1888–9; and *J.S.C.I.*, 1889, 575). From these he concluded that flax cellulose could be distinguished from cotton by the fact that it reduces neutral silver nitrate solution when boiled with it. Our experiments with *pure flax cellulose*, as yielded by the method of grass bleaching and very carefully prepared silver nitrate, gave entirely negative results, no reduction whatever being observed.

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* The flax having been subjected to the retting process, it will be more satisfactory to obtain results with unaltered products as a basis for the further investigation of the flax constituents.

We can only explain the reduction of the silver salt observed by assuming that Godeffroy experimented with imperfectly purified flax cellulose, retaining a portion of the constituents we have been describing; their entire removal without injuring the cellulose is a matter of great difficulty, as shown in their resistance to drastic reagents, both alkalis and oxidants. From our experience of the methods of bleaching adopted in the north of Ireland, we know, however, that their complete removal is a matter of daily practice, and our investigations of the product, that is, pure flax cellulose, comparatively with cotton cellulose, have failed so far to reveal any chemical difference between them. Oxidised with nitric acid under similar conditions, they yield oxycellulose and oxalic acid in identical proportions: in this, and with the experimental evidence before us, we can only conclude that linen and cotton celluloses are substantially identical.

Cellulose oxidised with alkaline permanganate yields, besides oxycellulose and oxalic and carbonic acids, intermediate products of aldehydic character. These when isolated are hygroscopic, with a strong odour of caramel, and yield furfuraldehyde on hydrolysis. From 22·6 grams of flax cellulose treated with 50 grams of potassium permanganate, dissolved with 25 grams of sodium hydrate in 400 c.c. of water, the temperature of the reduction being 40—50°, we obtained—

	Grams.	Per cent.
Oxycellulose	10·5	46·4
Intermediate products ..	3·5	15·5
Oxalic acid	4·3	19·4
Volatile acid	Equivalent to 0·12 gram Na_2O.	

Further researches in the various directions opened out by these investigations are in progress.

In conclusion, we beg to acknowledge our obligations to Mr. C. C. Connor, M.A., of Belfast, and Mr. R. N. Davies, of the Apothecaries' Hall, for much kind assistance in connection with this work.

XIII.—*Milk of Abnormal Quality.*

By FREDERICK JAMES LLOYD, F.I.C.

PERHAPS some apology is needed for bringing these notes before the Chemical Society, which is mainly concerned with the recondite investigations of those who are extending the boundaries of chemical science. My apology is, that the following facts not only materially affect views at present universally accepted as to the limits in the composition of genuine milk, but are also interesting physiologically.

On the 13th of November last, among some samples of milk forwarded for analysis, were two marked No. 40, which gave the results shown in the accompanying table. On the 19th, further samples were received from the same source, with a message that the former samples came from the sender's own cows, as also the samples then forwarded. Two of these, marked No. 41, gave the results shown in the table. I then visited the sheds, saw these cows, Nos. 40 and 41, obtained full particulars as to their feeding, and requested further samples, which reached me on the 22nd November. The analyses of these confirmed the previous results. Periodical analyses have since been made of the milk from these cows, with the following results (see table, p. 202).

The fat estimations have, in several cases, been made in more than one way, whilst all have been calculated by Fleischmann's formula from the total solids and specific gravity. The results have varied not more than 0·15 per cent., and seldom so much as that. Some of the milks were passed through a separator to determine if the fat, as estimated, could be removed as cream. This was so. The separated milks, upon analysis, confirmed the analyses of the whole milk as to the percentage of solids other than fat. The ash has been estimated on nine occasions, and gave 0·70, 0·76, 0·78, 0·78, 0·78, 0·80, 0·80, 0·84, 0·86. The utmost precaution was taken to ensure perfect combustion of the carbon.

Some complete analyses of the milk were made to discover whether the loss fell on any special constituent or on all alike.

The following are the results obtained:—

Composition of the Milk.

Yield of milk.		Date.	No. 40.						No. 41.					
			Morning.			Evening.			Morning.			Evening.		
40	41		Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.	Fat.	Other solids.	Total solids.
33 lbs.	37 lbs.	13th Nov.	3·41	8·47	11·88	5·71	8·63	14·34	—	—	—	—	—	—
—	—	19th „	—	—	—	—	—	—	3·80	8·24	12·04	4·54	8·10	12·64
—	—	22nd „	3·39	8·39	11·78	4·50	8·38	12·88	3·80	8·38	12·18	4·61	8·41	13·02
22 „	25 „	5th Dec.	3·44	8·28	11·72	5·12	8·48	13·60	3·07	8·21	11·28	4·50	8·52	13·02
—	—	10th „	2·17	7·87	10·04	4·68	8·30	12·98	3·13	8·19	11·32	5·13	8·25	13·38
15 „	22 „	17th „	2·98	7·58	10·56	3·86	8·14	12·00	3·27	8·27	11·54	4·26	8·26	12·52
8 „	18 „	7th Jan.	2·70	7·50	10·20	3·64	7·68	11·32	3·93	8·13	12·06	4·95	8·19	13·14

Complete Analyses.

	No. 40. 25th Nov. Morn.	No. 40. 25th Nov. Even.	No. 40. 5th Dec. Even.	No. 41. 25th Nov. Morn.	No. 41. 25th Nov. Even.	No. 41. 5th Dec. Even.	Average.
Fat	3·39	4·50	5·12	3·80	4·61	4·50	4·32
Casein.....	2·54	2·78	2·64	2·75	2·69	2·76	2·69
Albumin ...	0·39	0·29	0·24	0·45	0·45	0·26	0·35
Other N constituents*	—	—	0·44		—	0·42	0·43
Sugar......	4·76	4·55	4·36	5·11	4·43	4·30	4·19
Ash	0·70	0·76	0·80		0·84	0·78	0·78
	11·78	12·88	13·60	12·18	13·02	13·02	12·76
Solids other than fat..	8·39	8·38	8·48	8·38	8·41	8·52	8·44

* Nitrogen determined × 6·25.

The composition of the solids other than fat of good milk, judging from the preliminary results of experiments still in progress, may be taken to be as under. By deducting one-twelfth (the amount of solids other than fat, lacking in the milks under consideration), the remainder would have the composition also here shown.

	Normal composition of solids other than fat.	11/12th thereof.
Casein	3·00	2·75
Albumin	0·38	0·35
Other nitrogenous bodies	0·36	0·33
Sugar................	4·56	4·16
Ash	0·70	0·64
	9·00	8·23

Upon comparing these last figures with those of the complete milk analyses, it will be seen that they agree closely; hence the falling off has been equally distributed over both the caseïn, sugar, and other constituents, except the ash.

Some of the worst of these milks were drawn in my presence, by one milker, and the samples taken by me then. When not present myself, the owner of the cows supervised the milking and sample-taking, being deeply interested in the results of the inquiry. Hence the purity of the samples cannot be doubted.

What then is the cause of the abnormal results? Three causes appear probable. 1st, that the cows were suffering from a disease which, though at first unnoticeable, would, in time, become manifest.

But the cows have, as yet, shown no sign of disease. 2nd. That the food they received was either insufficient or ill-apportioned in its constituents. This, however, was not the case; the food was ample, and had been most carefully apportioned. As all the cows in the shed were receiving the same food, on each occasion of taking samples other cows were milked, and their milk analysed. But in no single instance has any other cow in the shed given milk which differed in any way from rich normal milk. To make more certain, the milk ot the whole shed was mixed, and a sample of the mixed milk analysed. The solids other than fat have only once (6th January) fallen below 9 per cent. Hence, the food was not at fault, even assuming, which is doubtful, that the food could affect the milk to such an extent. The third and last explanation, and the conclusion to which we are forced, is that owing to some inherent quality of these animals, the normal composition of their milk is such as has never before been recorded. They are cross-bred shorthorns, and No. 41 appears to have Dutch blood in her. But No. 40 has no appearance of foreign blood, and is to all intents and purposes a shorthorn. The animals are the property of Mr. A. Tisdall, of Holland Park Dairy, Kensington, who has retained them mainly for the purpose of this investigation.

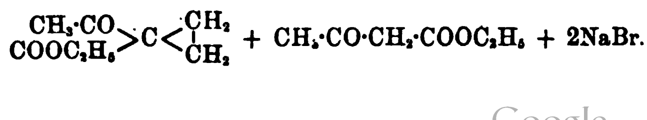
The quantity of milk they yield has not been large, and is decreasing rapidly.

XIV.—*Ethyl $\alpha\alpha_1$-Diacetyladipate.*

By W. H. PERKIN, Jun., Ph.D.

ETHYL sodioacetoacetate and ethylene bromide, when heated together, react readily with elimination of sodium bromide and formation of an almost colourless oil, which consists for the most part of two substances, mixed always with varying quantities of unchanged ethylene bromide and ethyl acetoacetate.

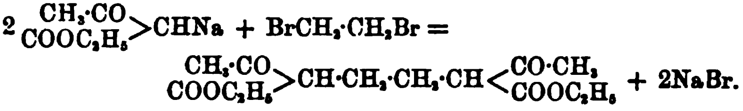
The first of these (which has already been described in detail in this Journal, 1885, **47**, 801; 1887, **51**, 820) is ethyl acetyltrimethylenecarboxylate, produced according to the equation—



$$2\,\begin{matrix}\mathrm{CH_3\cdot CO}\\ \mathrm{COOC_2H_5}\end{matrix}\!>\mathrm{CHNa} + \mathrm{BrCH_2\cdot CH_2Br} =$$

$$\begin{matrix}\mathrm{CH_3\cdot CO}\\ \mathrm{COOC_2H_5}\end{matrix}\!>\mathrm{C}<\!\begin{matrix}\mathrm{CH_2}\\ |\\ \mathrm{CH_2}\end{matrix} + \mathrm{CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5} + 2\mathrm{NaBr}.$$

The second substance, which has been called ethyl $\alpha\alpha_1$-diacetyladipate, is the product of the direct action of 1 mol. of ethylene bromide on 2 mols. of ethyl sodioacetoacetate, thus:—



$$2\left.\begin{matrix}\mathrm{CH_3\cdot CO}\\\mathrm{COOC_2H_5}\end{matrix}\right>\mathrm{CHNa} + \mathrm{BrCH_2\cdot CH_2Br} = \left.\begin{matrix}\mathrm{CH_3\cdot CO}\\\mathrm{COOC_2H_5}\end{matrix}\right>\mathrm{CH\cdot CH_2\cdot CH_2\cdot CH}\left<\begin{matrix}\mathrm{CO\cdot CH_3}\\\mathrm{COOC_2H_5}\end{matrix}\right. + 2\mathrm{NaBr}.$$

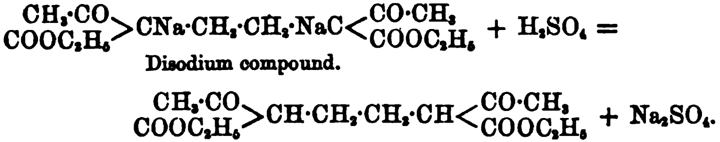
Some time since, I carried out, in conjunction with M. Obrembsky (*Berichte*, **19**, 2045), a short investigation of this substance, in the course of which we obtained several interesting derivatives; these however, we were then able to examine only superficially.

During the progress of some researches on the internal condensation of diketones, on which I am at present engaged, it became necessary to repeat all the experiments originally carried out with ethyl diacetyladipate, and also to institute a number of new ones; and I beg now to lay the results obtained before the Society.

Ethyl diacetyladipate cannot be separated by fractional distillation from the ethyl acetyltrimethylenecarboxylate and other impurities which accompany it, as by this treatment it undergoes a more or less complete decomposition even when distilled under greatly reduced pressure (50 mm.); an almost perfect separation may, however, be accomplished by distilling the crude product obtained in the action of ethylene bromide on ethyl sodioacetoacetate in a current of steam. By this treatment, all the ethyl acetyltrimethylenecarboxylate as well as unchanged ethylene bromide and ethyl acetoacetate pass over along with the water, leaving in the retort a thick, oily residue, which consists of slightly impure ethyl diacetyladipate.

From this, pure ethyl diacetyladipate may be obtained by two methods:—

I. The crude substance, dissolved in ether, is treated with sodium ethylate, and the precipitated disodium-compound collected, washed free from impurities, and decomposed by an acid—

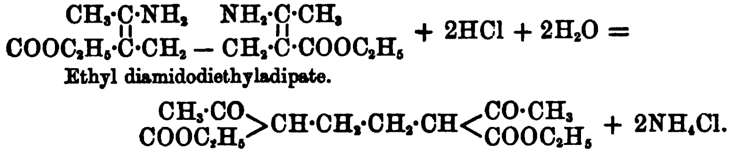


$$\left.\begin{matrix}\mathrm{CH_3\cdot CO}\\\mathrm{COOC_2H_5}\end{matrix}\right>\mathrm{CNa\cdot CH_2\cdot CH_2\cdot NaC}\left<\begin{matrix}\mathrm{CO\cdot CH_3}\\\mathrm{COOC_2H_5}\end{matrix}\right. + \mathrm{H_2SO_4} = \left.\begin{matrix}\mathrm{CH_3\cdot CO}\\\mathrm{COOC_2H_5}\end{matrix}\right>\mathrm{CH\cdot CH_2\cdot CH_2\cdot CH}\left<\begin{matrix}\mathrm{CO\cdot CH_3}\\\mathrm{COOC_2H_5}\end{matrix}\right. + \mathrm{Na_2SO_4}.$$

Disodium compound.

Ethyl diacetyladipate.

II. The crude product is treated with concentrated alcoholic ammonia, the crystalline diamido-compound which separates collected, purified by recrystallisation, and decomposed by dilute hydrochloric acid—



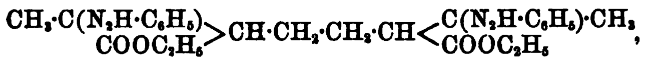
$$\begin{matrix}CH_3\cdot C\cdot NH_2 & NH_2\cdot C\cdot CH_3\\ \| & \| \\ COOC_2H_5\cdot C\cdot CH_2 - & CH_2\cdot C\cdot COOC_2H_5\end{matrix} + 2HCl + 2H_2O =$$

Ethyl diamidodiethyladipate.

$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>CH\cdot CH_2\cdot CH_2\cdot CH<\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix} + 2NH_4Cl.$$

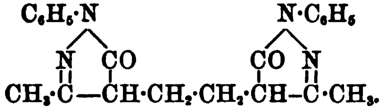
Pure ethyl diacetyladipate is a thick, colourless oil, possessing properties very similar to those noticed in the case of mono-substituted derivatives of ethyl acetoacetate.

When heated with 2 mols. of phenylhydrazine on a water-bath, it yields as primary product, ethyl diphenylhydrazinediacetyladipate,



$$\begin{matrix}CH_3\cdot C(N_2H\cdot C_6H_5)\\ COOC_2H_5\end{matrix}\!>CH\cdot CH_2\cdot CH_2\cdot CH<\!\begin{matrix}C(N_2H\cdot C_6H_5)\cdot CH_3\\ COOC_2H_5\end{matrix},$$

a yellowish-white, crystalline substance which melts at 145°, and, when heated, readily loses 2 mols. of alcohol being converted into bisphenylmethylmethylenepyrazolone,



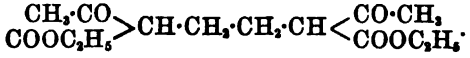
This pyrazolone-derivative crystallises from acetic acid in white needles, which are almost insoluble in most organic solvents, and do not melt at 250°. In its other properties this interesting substance shows considerable similarity to other pyrazolones substituted in the methylene-group.

The careful study of the products of the distillation of ethyl diacetyladipate has led to very interesting results.

This substance, when fractioned under diminished pressure (225 mm.), distils, with apparently very slight decomposition, as a yellow oil, only a small quantity of a thick, dark-coloured residue remaining in the retort. The oily distillate, on repeated distillation, yields a large fraction boiling constantly at 230—231° (225 mm.), which, on analysis, gives numbers agreeing with the formula $C_{14}H_{20}O_5$.

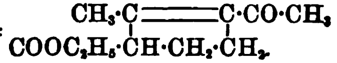
Careful investigation has shown that this apparently pure product is a mixture very probably of three substances, namely :—

I. Ethyl diacetyladipate =



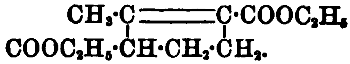
$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>CH\cdot CH_2\cdot CH_2\cdot CH<\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix}.$$

II. Ethyl methyldihydropentene-methylketonecarboxylate* =



$$\begin{matrix}CH_3\cdot C & = & C\cdot CO\cdot CH_3\\ | & & | \\ COOC_2H_5\cdot CH & \cdot CH_2\cdot & CH_2.\end{matrix}$$

III. Ethyl methyldihydropentene-dicarboxylate* .... =



$$\begin{matrix}CH_3\cdot C & = & C\cdot COOC_2H_5\\ | & & | \\ COOC_2H_5\cdot CH & \cdot CH_2\cdot & CH_2.\end{matrix}$$

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* See "Nomenclature of unsaturated closed carbon chains, p. 212."

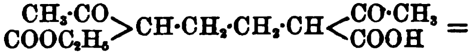
In order to separate these substances, the crude oil is dissolved in ether, and well shaken with a dilute solution of potassium hydrate, by which means a considerable quantity of a dark-coloured substance is removed. The oil is then redistilled, treated again with potassium hydrate, and the operation repeated several times until the potash has no further action on the oil.

The alkaline extract, on being acidified, deposits a quantity of a dark-brown oil, which it was found impossible to purify.

On distilling this crude substance under reduced pressure (100 mm.), carbonic anhydride is first given off and then a yellow oil distils, leaving a fairly large amount of a dark residue in the retort.

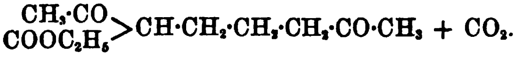
The distillate, on repeated refractionation, distils for the most part between 195° and 200° (100 mm.), and on analysis gave numbers agreeing with the formula $C_{11}H_{18}O_4$. This new substance, on hydrolysis with alcoholic potash, deposits a quantity of potassium carbonate, and yields two principal products, namely, methyldehydropentene methyl ketone and ω-acetylvalerianic acid.

These facts can be explained on the supposition that on distilling ethyl diacetyladipate, a certain amount passes over unchanged; on subsequent treatment with potassium hydrate, this is partially hydrolysed and passes into solution as potassium ethyl diacetyladipate. The free ethyl hydrogen salt, liberated by the addition of an acid, is decomposed on distillation into carbonic acid and ethyl $\alpha\omega$-diacetylvalerate, thus:—



$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}{>}CH\cdot CH_2\cdot CH_2\cdot CH{<}\begin{matrix}CO\cdot CH_3\\ COOH\end{matrix} =$$

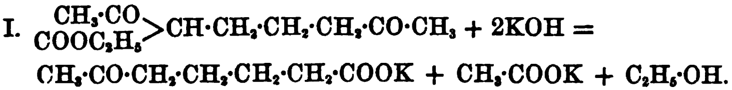
Ethyl hydrogen diacetyladipate.



$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}{>}CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 + CO_2.$$

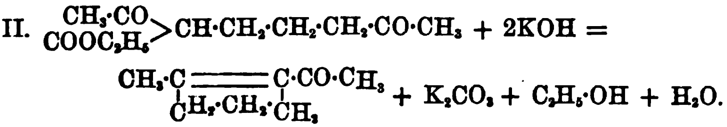
Ethyl $\alpha\omega$-diacetylvalerate.

Ethyl $\alpha\omega$-diacetylvalerate, on hydrolysis, yields ω-acetylvalerianic acid and methyldihydropentene methyl ketone, thus:—



$$\text{I.}\quad \begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}{>}CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 + 2KOH =$$
$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot COOK + CH_3\cdot COOK + C_2H_5\cdot OH.$$

Potassium $\alpha\omega$-acetylvalerate.



$$\text{II.}\quad \begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}{>}CH\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3 + 2KOH =$$
$$\begin{array}{l}CH_3\cdot C{=\!=\!=\!=}C\cdot CO\cdot CH_3\\ \quad | \qquad\qquad\quad |\\ \quad CH_2\cdot CH_2\cdot CH_2\end{array} + K_2CO_3 + C_2H_5\cdot OH + H_2O.$$

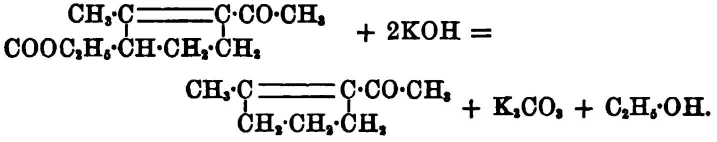
Methyldihydropentene methyl ketone.

It is very probable that this repeated fractionation and treatment of the crude product of the distillation of ethyl diacetyladipate with potash removes other substances besides unchanged ethyl diacetyladipate; but no attempts have been made to isolate them.

The oily substance, which had been left unattacked by the potash, and which forms by far the greater portion of the whole, distilled almost constantly at 191—192° (35 mm.), and gave on analysis numbers agreeing approximately with the formula $C_{11}H_{16}O_3$.

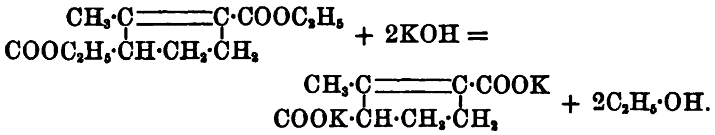
This oil consists of two substances represented above by formulæ II and III, the latter being present in very small quantity.

On hydrolysis, this oil yields methyldihydropentene methyl ketone and small quantities of methyldihydropentenedicarboxylic acid. The former is produced from ethyl methyldihydropentenemethylketonecarboxylate, thus:—



$$\begin{array}{l} CH_3\cdot C = C\cdot CO\cdot CH_3 \\ COOC_2H_5\cdot CH\cdot CH_2\cdot CH_2 \end{array} + 2KOH = \begin{array}{l} CH_3\cdot C = C\cdot CO\cdot CH_3 \\ CH_2\cdot CH_2\cdot CH_2 \end{array} + K_2CO_3 + C_2H_5\cdot OH.$$

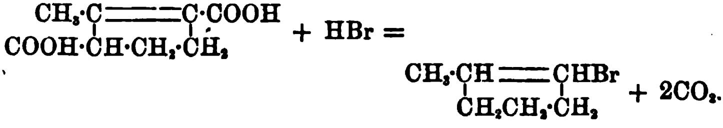
The latter results from the hydrolysis of ethyl methyldihydropentenedicarboxylate:—



$$\begin{array}{l} CH_3\cdot C = C\cdot COOC_2H_5 \\ COOC_2H_5\cdot CH\cdot CH_2\cdot CH_2 \end{array} + 2KOH = \begin{array}{l} CH_3\cdot C = C\cdot COOK \\ COOK\cdot CH\cdot CH_2\cdot CH_2 \end{array} + 2C_2H_5\cdot OH.$$

Methyldihydropentene methyl ketone is a colourless, mobile oil, possessing in a most pronounced manner the odour of peppermint. It boils constantly at 191° (760 mm.) and enters into a number of extremely interesting reactions, which will be fully described later on.

Methyldihydropentenedicarboxylic acid crystallises from water in large, silky needles which melt at 188°. It combines with bromine and gives Baeyer's permanganate test, and behaves in all respects like an unsaturated chain acid. When heated with hydrobromic acid, it is decomposed with evolution of carbon dioxide and formation of a neutral brominated oil, which appears to be methylbromopentamethylene—

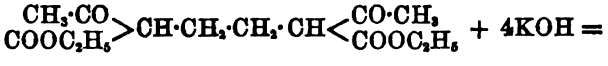


$$\begin{array}{l} CH_3\cdot C = C\cdot COOH \\ COOH\cdot CH\cdot CH_2\cdot CH_2 \end{array} + HBr = \begin{array}{l} CH_3\cdot CH = CHBr \\ CH_2CH_2\cdot CH_2 \end{array} + 2CO_2.$$

It is unfortunate that the amount of this acid obtained by the above reaction is so small (1 per cent.); as, owing to its peculiar structure, many interesting results might be expected from the further study of its properties.

The hydrolysis of ethyl diacetyladipate by means of alcoholic potash has been carefully studied by Dr. Marshall and myself, and a number of interesting substances have been obtained.

If ethyl diacetyladipate is boiled only for a short time with alcoholic potash,* $\omega\omega_1$-diacetylbutane is the principal product formed, thus:—



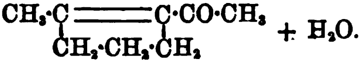
$$\begin{array}{l}\mathrm{CH_3\cdot CO}\\\mathrm{COOC_2H_5}\end{array}\!\!>\mathrm{CH\cdot CH_2\cdot CH_2\cdot CH}<\!\!\begin{array}{l}\mathrm{CO\cdot CH_3}\\\mathrm{COOC_2H_5}\end{array} + 4\mathrm{KOH} =$$

$$\mathrm{CH_3\cdot CO\cdot[CH_2]_4\cdot CO\cdot CH_3} + 2\mathrm{K_2CO_3} + \mathrm{C_2H_5\cdot OH}.$$

Diacetylbutane.

This new diketone, which is the next lowest in the series to diacetylpentane, described a short time since by Dr. Kipping and myself, is a colourless crystalline mass, melting at 43—44°. It is characterised by the ease with which it loses 1 mol. H_2O with formation of methyldihydropentene methyl ketone, thus:—

$$\mathrm{CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3} =$$

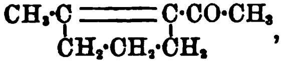


$$\begin{array}{l}\mathrm{CH_3\cdot C{=\!=\!=}C\cdot CO\cdot CH_3}\\\quad\mathrm{CH_2\cdot CH_2\cdot CH_2}\end{array} + \mathrm{H_2O}.$$

this change taking place on simply boiling it with alcoholic potash.

If, therefore, ethyl diacetyladipate is boiled for some time with an excess of a strong solution of potash in alcohol, the whole of the diketone is decomposed, methyldihydropentene methyl ketone being the sole product; this reaction serving as the best method for preparing this substance. That it is identical with the methyldihydropentene methyl ketone obtained by the hydrolysis of the oil $C_{11}H_{16}O_3$, as described above, is shown by the fact that both products boil at 191° and both yield an oxime melting at 86°.

As by this method considerable quantities of the ketone could be obtained with comparative facility, numerous experiments were tried with it, with the object of obtaining data in proof of the formula

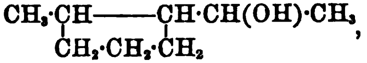


$\begin{array}{l}\mathrm{CH_3\cdot C{=\!=\!=}C\cdot CO\cdot CH_3}\\\quad\mathrm{CH_2\cdot CH_2\cdot CH_2}\end{array}$, assigned to it throughout this paper.

When subjected to the action of excess of sodium in moist ethereal solution, this ketone, $C_8H_{12}O$, takes up 4 atoms of hydrogen and is converted into a well characterised alcohol,

---

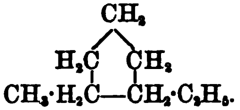
* Prof. v. Baeyer has called my attention to the nomenclature used in these researches, and suggests that it is better to designate diketones of the formula $\mathrm{CH_3\cdot CO\cdot[CH_2]_n\cdot CO\cdot CH_3}$ as $\omega\omega_1$-derivatives instead of $\alpha\omega$-derivatives. $\alpha\omega$-Diacetylpentane and the other similarly constituted diketones lately described by Dr. Kipping and myself should therefore be called $\omega\omega_1$-diacetylpentane, &c.



$$\begin{array}{l} CH_3\cdot CH\text{———}CH\cdot CH(OH)\cdot CH_3 \\ \quad\; CH_2\cdot CH_2\cdot CH_2 \end{array},$$

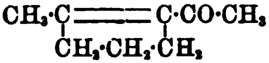
which has received the name methylpentamethylene methyl carbinol.

This alcohol is a colourless oil, boiling constantly at 180°. Its acetate, $C_8H_{15}O(C_2H_3O)$, boils at 145—150° (130 mm.). Methyl pentamethylene methyl carbinol is not acted on by boiling with alcohol and excess of sodium, and it is, therefore, evidently a saturated compound. Fuming hydriodic acid converts it into its iodide, $C_8H_{15}I$, and this, when heated with fuming hydriodic acid and amorphous phosphorus at 250° for several hours, is reduced to methylethylpentamethylene (1.2),



It is a colourless oil boiling constantly at 124° and having an odour closely resembling that of the normal paraffins.

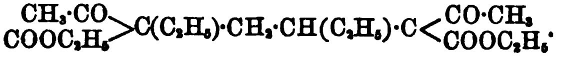
In studying these reactions one cannot but be struck with the great similarity existing between methyldihydropentene methyl ketone and the product of the internal condensation of diacetylpentane (methyltetrahydrobenzene methyl ketone), described by Dr. Kipping and myself some time since. Both these substances form oximes; both, on reduction with sodium in moist ethereal solution, take up 4 atoms of hydrogen and yield alcohols which, on treatment with hydriodic acid, are reduced to saturated hydrocarbons of the general formula C_nH_{2n}.

The arguments, based on these reactions, which were used in discussing the formula of methyltetrahydrobenzene methyl ketone (this vol., p. 14) apply equally well to the present case, and need not be again repeated. There is, however, one confirmatory test which was used in determining the constitution of methyltetrahydrobenzene methyl ketone which we have unfortunately not been able to apply to the dihydropentene-derivative. If the formula  $\begin{array}{l} CH_3\cdot C\text{====}C\cdot CO\cdot CH_3 \\ \quad\; CH_2\cdot CH_2\cdot CH_2 \end{array}$ represents the constitution of methyldihydropentene methyl ketone, it is obvious that diethyldiacetylbutane,

$$CH_3\cdot CO\cdot CH(C_2H_5)\cdot CH_2\cdot CH_2\cdot CH(C_2H_5)\cdot CO\cdot CH_3.$$

could not yield a similar condensation-product, and this fact, if demonstrated, would go far to prove the formula given above.

In order to obtain this substance, it was necessary first to prepare ethylic diethyldiacetyladipate,

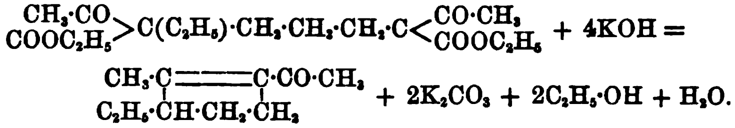


$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>\!C(C_2H_5)\cdot CH_2\cdot CH(C_2H_5)\cdot C\!<\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix}.$$

As this compound was not formed by the action of ethylene bromide on ethyl sodioethylacetoacetate, we endeavoured to obtain it by treating the disodium compound of ethyl diacetyladipate with ethyl iodide.

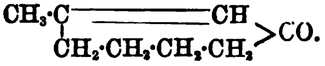
The product of the reaction, on hydrolysis, gave a neutral oil, which, on fractioning first under reduced pressure and then under the ordinary pressure, distilled for the most part between 200° and 260°.

From this crude product, a substance was readily obtained boiling at 210—215°, which on analysis gave numbers agreeing with the formula $C_{10}H_{16}O$; this oil, when treated with hydroxylamine, gave an oxime $C_{10}H_{17}NO$. The general properties of the substance, and especially the strong odour of peppermint, agree so closely with those of methyldihydropentene methyl ketone that there can be no doubt that this new compound is simply the ethyl-derivative of this ketone, produced by the hydrolysis of ethylic monethyldiacetyladipate.



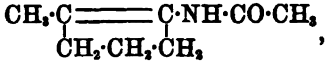
A second fraction, 250—255°, gave, on analysis, numbers agreeing only approximately with the formula of diethyldiacetylbutane, and owing to the very small quantity of this substance produced, we were unable to purify it further.

Some experiments were next made with the object of proving the presence of an acetyl-group in methyldihydropentene methyl ketone, as this would in a great measure confirm the formula given to this substance, and more particularly distinguish between this and the formula—

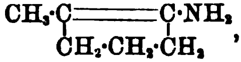


(Compare formula for methyltetrahydrobenzene methyl ketone, this vol., p. 14.) The oxime $C_8H_{13}NO$ was heated in a sealed tube with a mixture of acetic acid, acetic anhydride, and hydrogen chloride at 100° for two hours.

According to the beautiful researches of Beckmann on "intermolecular change in oximes," this experiment should have converted the oxime into methyldihydropenteneacetamide,

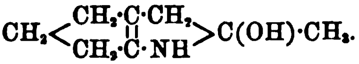


$$\begin{array}{l} CH_3{\cdot}C\!=\!\!=\!\!=\!\!=\!C{\cdot}NH{\cdot}CO{\cdot}CH_3 \\ \quad CH_2{\cdot}CH_2{\cdot}CH_2 \end{array},$$

a substance which on hydrolysis should have yielded methyldihydropenteneamine,  $\begin{array}{l} CH_3{\cdot}C\!=\!\!=\!\!=\!C{\cdot}NH_2 \\ \quad CH_2{\cdot}CH_2{\cdot}CH_2 \end{array}$, and acetic acid, as described in detail in the body of this paper.

From the product of this reaction a remarkable base was isolated, which boiled constantly at 164—165°, and volatilised readily with steam; on analysis it gave numbers agreeing with the formula $C_8H_{13}NO$, and behaved in all its reactions like a strong base. The platinochloride $(C_8H_{13}NO)_2,H_2PtCl_6$, crystallises from water in beautiful, orange-red prisms, and is very stable.

This substance is evidently not methyldihydropenteneacetamide, as even prolonged boiling with dilute hydrochloric acid does not appear to affect it, and it is thought possible that by intermolecular change the oxime has been converted into a ring-derivative having the formula—

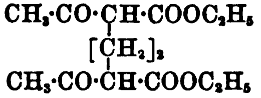


$$CH_2{<}\begin{array}{l} CH_2{\cdot}C{\cdot}CH_2 \\ CH_2{\cdot}C{\cdot}NH \end{array}{>}C(OH){\cdot}CH_3.$$

I am at present engaged in a further study of this base.

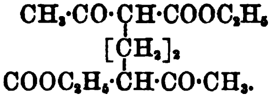
Crude ethyl diacetyladipate, which results from distilling the product of the action of ethylene bromide on ethyl sodioacetoacetate with steam, appears to be a very fairly pure substance, as is proved not only by analysis, but also from the fact that when treated with phenylhydrazine a very large yield of phenylhydrazine-derivatives can be obtained. This is also borne out by the study of various other decompositions of this crude product, and yet, curiously enough, when treated with ammonia, even under the most varied conditions, only 30 per cent. of the theoretical yield of ethyl diimidodiethyladipate is obtained. As it was thought that this might be due to some secondary action of the ammonia, pure ethyl diacetyladipate (prepared from ethyl diimidodiethyladipate) was treated with alcoholic ammonia, with the result that over 90 per cent. of the theoretical amount of the crystalline diimido-compound was obtained.

This diimido-compound is extremely insoluble in cold alcohol, and an examination of the crude oily products contained in the mother liquors obtained by treating crude ethyl diacetyladipate with ammonia showed that it contained an imido-compound, which, however, could not be obtained in a pure state. These and other considerations make it appear probable that crude ethyl diacetyladipate contains two structurally physical isomerides, namely:—



$$\begin{matrix}CH_3\cdot CO\cdot CH\cdot COOC_2H_5\\ [CH_2]_2\\ CH_3\cdot CO\cdot CH\cdot COOC_2H_5\end{matrix}$$

and



$$\begin{matrix}CH_3\cdot CO\cdot CH\cdot COOC_2H_5\\ [CH_2]_2\\ COOC_2H_5\cdot CH\cdot CO\cdot CH_3.\end{matrix}$$

a supposition supported to some extent by recent work on the disubstituted succinic acids.

A somewhat similar case has been noticed in studying the formation of ethyl dibenzoylsuccinate, $\begin{matrix}C_6H_5\cdot CO\\ COOC_2H_5\end{matrix}>CH\cdot CH<\begin{matrix}CO\cdot C_6H_5\\ COOC_2H_5\end{matrix}$, by the action of iodine on the sodium compound of ethyl benzoylacetate. The ethereal salt usually obtained melts at 128°, but under certain conditions, which have not as yet been clearly established, an isomeric substance, m.p. 154°, results.

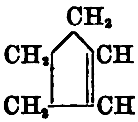
It is hoped that further investigation will clear up this interesting point.

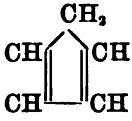
NOMENCLATURE OF UNSATURATED CLOSED CARBON CHAINS.

Considerable difficulty attaches to the question of the nomenclature of partially saturated ring-derivatives, such as occur in this and the following papers.

In previous researches on the synthetical formation of closed carbon chains, only derivatives of fully saturated rings have been dealt with; such were named tri-, tetra-, penta-, hexa-methylene-derivatives, according to the number of "methylene" groups contained in the ring.

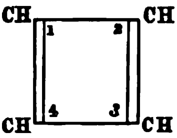
Formulæ derived from such methylene rings by the abstraction of pairs of hydrogen-atoms might be distinguished by prefixing the words dehydro-, didehydro-, tridehydro-, &c., according to the number of pairs of hydrogen-atoms removed.

Thus the ring  would be dehydropentamethylene;

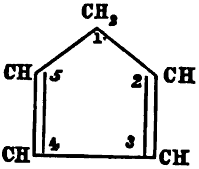
the ring  would be didehydropentamethylene, &c

Quite apart from the inconvenient length of such words, and the difficulty of pronouncing them, the use of the word "dehydro-" in this sense might easily cause confusion, on account of the fact that this term usually implies "elimination of water."

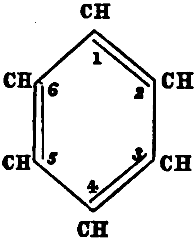
A system of nomenclature which avoids this difficulty, and which is also of general applicability, may, it seems to me, be obtained by naming the *entirely unsaturated* rings, containing *double linkings*, by following scheme, in which the position of the double linkings is shown by prefixing the sign Δ with the commencing number of the double linkings, reading in the direction of the hands of a watch, (compare Baeyer, *Annalen*, **245**, 111).



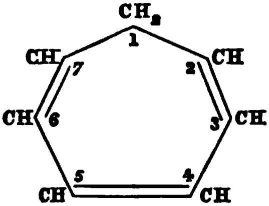
$\Delta^{2\cdot4}$-*Tetrene.*



$\Delta^{2\cdot4}$-*Pentene.*



$\Delta^{1\cdot3\cdot5}$-*Hexene* (Benzene).



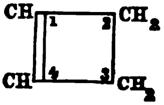
$\Delta^{2\cdot4\cdot6}$-*Heptene.*

&c.

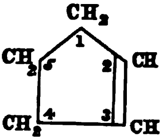
These names ending in *-ene* could not be confounded with unsaturated chain derivatives, because these have always received names ending in -ylene, such as ethylene, tetrylene, pentylene, &c.

Partially saturated derivatives of the above rings would then be named according to the number of hydrogen-atoms taken up; the position of the remaining double likings might be (as above) represented by Δ, with the number attached at which the double linking starts, counting always in the direction of the hands of a watch.

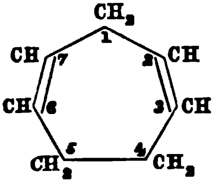
The following examples illustrate this point clearly:—



Δ^4-Dihydrotetrene.



Δ^2-Dihydropentene.

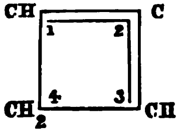


$\Delta^{2\cdot6}$-Dihydroheptene.

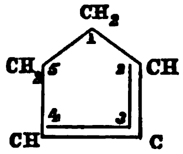
&c.

The fully saturated rings would be methylene-derivatives, as before.

Isomeric hydrocarbons, with double linkings in positions different from the above, could, if prepared, of course be similarly named, thus :—



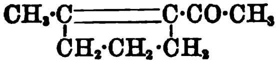
$\Delta^{1\cdot 2}$-Tetrene.



$\Delta^{2\cdot 3}$-Pentene.

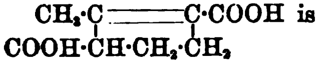
&c.

The substances described in this paper fall under the heading of pentene-derivatives.



$$\begin{array}{l} CH_3\cdot C{=\!=\!=\!=\!=}C\cdot CO\cdot CH_3 \\ \;\;|\qquad\quad\;\; | \\ CH_2\cdot CH_2\cdot CH_2 \end{array}$$

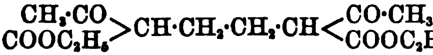
is Δ^2 methyldihydropentene methyl ketone (2, 3).



$$\begin{array}{r} CH_3\cdot C{=\!=\!=\!=\!=}C\cdot COOH \\ |\qquad\quad\;\; | \qquad\qquad \\ COOH\cdot CH\cdot CH_2\cdot CH_2 \end{array}$$

is Δ^2 methyldihydropentenedicarboxylic acid (2, 3, 1).

&c., the numbers placed after the name in a bracket referring to the position of the side chains (Trans., 1885, **47**, 801). In most cases, where there is no fear of confusion, these numbers, as well as the symbol Δ, may be left out, as has been shown in the body of this paper.



ETHYL $\alpha_1\alpha_2$-DIACETYLADIPATE, $\begin{matrix} CH_3\cdot CO \\ COOC_2H_5 \end{matrix}\!\!>CH\cdot CH_2\cdot CH_2\cdot CH<\!\!\begin{matrix} CO\cdot CH_3 \\ COOC_2H_5 \end{matrix}$.

In preparing this substance the following quantities are conveniently employed :—

Ethyl acetoacetate	260 grams.
Ethylene bromide	190 ,,
Sodium......................	46 ,,

The sodium is dissolved in 500 grams of absolute alcohol, the solution well cooled, and then the mixture of ethyl acetoacetate and ethylene bromide gradually added, the temperature being kept below 35° by repeatedly cooling with cold water. The resulting clear solution is then heated to boiling in a large flask connected with a reflux apparatus for five hours, the alcohol distilled off, sufficient water added to completely dissolve the cake of sodium bromide, and the oily layer which separates extracted three times with small quantities of ether.

The ethereal solution on evaporation deposits about 240 grams of a slightly brownish oil, which, besides ethyl diacetyladipate, contains considerable quantities of ethyl acetyltrimethylenecarboxylate, as well as unchanged ethyl acetoacetate and some ethylene bromide. In order to remove these, advantage is taken of the fact that ethyl diacetyladipate is not volatile with steam, whereas the other substances mentioned are readily carried over. The crude product is therefore submitted to rapid distillation in a current of steam, the operation being continued until no more oily drops are visible in the condensed water. The residue is extracted three times with ether, the ethereal solution washed twice with a dilute solution of sodium carbonate, dried over anhydrous potassium carbonate, filtered, and the ether distilled off.

In this way about 60 grams of a slightly brownish oil is obtained, which, after standing for some days over sulphuric acid in a vacuum, gave the following numbers on analysis:—

0·1330 gram substance gave 0·2910 gram CO_2 and 0·0920 gram H_2O.

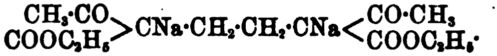
	Theory.		Found.	
C	58·74	per cent.	59·67	per cent.
H	7·69	„	7·69	„
O	33·57	„	32·64	„

Pure ethyl diacetyladipate may be readily prepared from this crude product by either of the following methods:—

I. By conversion into the disodium-derivative, and subsequent decomposition of the purified salt by dilute acids.
II. By the hydrolysis of ethyl diimidodiethyladipate.

These two methods will be given in detail in the following sections.

Disodium Compound of Ethyl Diacetyladipate,



$$\begin{matrix}CH_3{\cdot}CO\\ COOC_2H_5\end{matrix}{>}CNa{\cdot}CH_2{\cdot}CH_2{\cdot}CNa{<}\begin{matrix}CO{\cdot}CH_3\\ COOC_2H_5\end{matrix}.$$

This is best prepared in the following way:—

3·3 grams of sodium is dissolved in 30 grams of warm absolute alcohol, and the solution, while still warm, mixed with 50 grams of pure dry ether. 20 grams of crude ethyl diacetyladipate dissolved in 200 grams of pure dry ether is now added, and the yellow flocculent disodium compound, which immediately separates, rapidly filtered off, well washed with ether, and at once transferred to a vacuum desiccator.

The analysis of this compound gave the following numbers:—

I. 0·2884 gram substance gave (after ignition with H_2SO_4) 0·1190 gram Na_2SO_4.

II. 0·2605 gram substance gave (after ignition with H_2SO_4) 0·1062 gram Na_2SO_4.

	Theory.	Found.	
	$C_{14}H_{20}Na_2O_6$.	I.	II.
Na	13·94 p. c.	13·37	13·23 p. c.

This disodium compound is readily soluble in alcohol, almost insoluble in ether. It is decomposed at once by dilute acids, with regeneration of ethyl diacetyladipate; water acts in the same way, but not so readily.

In preparing pure ethyl diacetyladipate, the disodium compound, after being freed from impurities by washing with ether, as explained above, is at once thrown into a considerable volume of very dilute hydrochloric acid, and the oily compound thus liberated extracted three times with pure ether. The ethereal solution, after washing with dilute sodium carbonate solution, and drying over potassium carbonate, is allowed to evaporate, when it deposits an almost colourless oil; this, after standing over sulphuric acid in a vacuum for 24 hours, was analysed with the following result:—

I. 0·2116 gram substance gave 0·4572 gram CO_2 and 0·1380 gram H_2O.

II. 0·2130 gram substance gave 0·4530 gram CO_2 and 0·1530 gram H_2O.

III. 0·1988 gram substance gave 0·4244 gram CO_2 and 0·1409 gram H_2O.

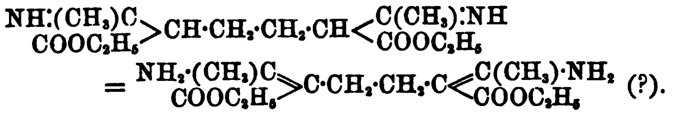
IV. 0·1226 gram substance gave 0·2632 gram CO_2 and 0·0921 gram H_2O.

		Found.			
	Theory.	I.	II.	III.	IV.
C	58·74	58·92	58·00	58·22	58·55
H	7·69	7·24	7·98	7·87	8·34
O........	33·57	33·84	34·02	33·91	33·11

Ethyl diacetyladipate is a thick, colourless oil, possessing a faint, fruity odour. It does not solidify when cooled to 0°. It is miscible with ether, alcohol, and most other organic solvents, almost insoluble in water, slightly soluble in dilute aqueous solutions of potassium and sodium hydrates. The addition of a drop of ferric chloride to the alcoholic solution gives an intense violet-red coloration. When agitated for some weeks with a saturated solution of sodium hydrogen sulphite, the ethereal salt gradually dissolves, forming a very readily soluble double compound. This, on the addition of dilute acids or carbonate of soda, deposits colourless, oily drops, which consist probably of regenerated ethyl diacetyladipate.

Ethyl diacetyladipate is readily hydrolysed by boiling with alcoholic potash, and in this way a number of interesting compounds have been obtained, which are described in the next paper.

Ethyl Diimidodiethyladipate,



$$\begin{matrix}NH{:}(CH_3)C\\COOC_2H_5\end{matrix}{>}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH{<}\begin{matrix}C(CH_3){:}NH\\COOC_2H_5\end{matrix}$$

$$= \begin{matrix}NH_2{\cdot}(CH_3)C\\COOC_2H_5\end{matrix}{>}C{\cdot}CH_2{\cdot}CH_2{\cdot}C{<}\begin{matrix}C(CH_3){\cdot}NH_2\\COOC_2H_5\end{matrix}\ (?).$$

This important compound is best prepared in the following way:—50 grams of crude ethyl diacetyladipate are dissolved in about 150—200 grams of absolute alcohol, and the solution thoroughly saturated with gaseous ammonia, the temperature being kept below 30° during the operation by means of cold water.

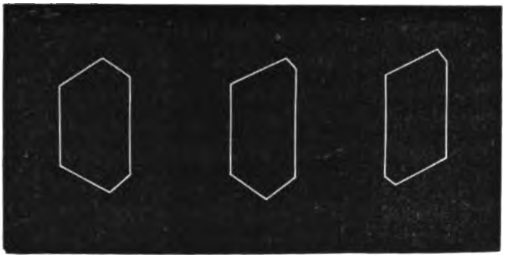
The solution on standing gradually deposits beautiful, glittering crystals, which, after 36 hours, are collected, well washed with alcohol, and dried on a porous plate.

The residual, beautifully white, glistening, crystalline mass, after recrystallisation from benzene, gave the following results on analysis:—

I. 0·1880 gram substance gave 0·4081 gram CO_2 and 0·1485 gram H_2O.
II. 0·1728 gram substance gave 0·3744 gram CO_2 and 0·1338 gram H_2O.
III. 0·1838 gram substance gave 16·5 c.c. N; $t = 14°$; bar. = 724 mm.

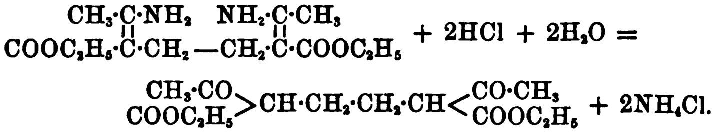
	Theory.	Found.			
	$C_{14}H_{24}N_2O_4$.	I.	II.	III.	
C	59·15 p. c.	59·20	59·09	—	p. c.
H	8·45 „	8·77	8·60	—	„
N	9·85 „	—	—	10·09	„

Ethyl diimidodiethyladipate melts at 173—174°. It is readily soluble in hot alcohol, benzene, and toluene, and crystallises from these solvents, on cooling, in beautiful, glittering plates or long, flat needles, which, when examined under the microscope, are seen to be of the following forms:—



Twin crystals were also sometimes noticed.

It is almost insoluble in water and only sparingly soluble in ether, light petroleum, or cold alcohol. Hydrochloric acid dissolves ethyl diimidodiethyladipate readily, especially on gentle warming; the addition of platinic chloride to the solution produces at first no precipitate, but on standing, glistening octahedra separate, which on examination were identified as crystals of ammonium platinochloride. This solution of ethyl diimidodiacetyladipate in hydrochloric acid remains clear for a considerable time, even when diluted with considerable quantities of water, but on gently warming on a water-bath, the liquid suddenly becomes turbid owing to the separation of minute particles of ethyl diacetyladipate, and the solution on boiling with alkalis gives off quantities of ammonia:—



$$\begin{matrix} & CH_3\cdot C\cdot NH_2 & NH_2\cdot C\cdot CH_3 & \\ & \| & \| & \\ COOC_2H_5\cdot & C\cdot CH_2 - & CH_2\cdot C & \cdot COOC_2H_5 \end{matrix} + 2HCl + 2H_2O =$$

$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!\!>CH\cdot CH_2\cdot CH_2\cdot CH<\!\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix} + 2NH_4Cl.$$

This decomposition serves as a ready means of preparing pure ethyl diacetyladipate from the crude product, without the necessity of using the disodium compound. For this purpose the finely-divided diimido-compound is agitated with just sufficient hydrochloric acid (sp. gr. 1·16) to dissolve it, the clear solution diluted with 3 vols. of water and warmed on a water-bath to about 80°. Long before the solution attains this temperature a cloudiness suddenly appears, and in a short time a thick, oily layer of ethyl diacetyladipate settles down in the aqueous solution.

This is extracted twice with pure ether, the ethereal solution washed with sodium carbonate, dried over potassium carbonate, and evaporated. The resulting colourless oil, after standing for some hours over sulphuric acid in a vacuum, consists of pure ethyl diacetyladipate, as the following analysis shows:—

0·1505 gram substance gave 0·1046 gram H_2O and 0·3228 gram CO_2.

	Theory. $C_{14}H_{22}O_6$.	Found.
C	58·74 per cent.	58·49 per cent.
H	7·69 ,,	7·72 ,,
O	33·56 ,,	33·79 ,,

This method is the most convenient for preparing pure ethyl diacetyladipate, although the yield obtained is only 30 per cent. of the crude product employed.

In preparing ethyl diimidodiethyladipate, as described above, rarely more than 30 per cent. of the crystalline substance is obtained, notwithstanding that the ethyl diacetyladipate employed could have contained only a small quantity of impurity, as shown by the yields of other derivatives obtained from it.

The mother liquors from the crystals were found on examination to contain a large quantity of an oily ammonium compound which could not be obtained in a pure state. In order, if possible, to improve the yield of ethyl diimidodiethyladipate, various experiments were tried, using not only different solvents, but also varying quantities of ammonia, but without success. If crude ethyl diacetyladipate is shaken with an excess of strong aqueous ammonia, and the solution allowed to stand for some days, the globules of oil gradually become more and more viscid and at last break up entirely into semi-solid particles. These are collected, freed from oil by spreading on a porous plate, and washed with alcohol. The colourless crystalline mass thus obtained is identical with the substance described above, and the yield is almost the same as that obtained with alcoholic ammonia.

As the yield of crystals by all methods was so small, it seemed probable that the ammonia exerted some secondary influence on the ethyl diacetyladipate, converting it possibly into an acid amide. In order to test this, 5 grams of pure ethyl diacetyladipate (prepared from ethyl diimidodiethyladipate) was dissolved in 20 grams of pure methyl alcohol, the solution saturated with ammonia and allowed to stand for 24 hours. The crystals of the diimido-compound thus formed were collected, washed with alcohol, and found to weigh 4·1 grams. The mother liquor, on evaporation at the ordinary temperature, deposited 0·53 gram of crystals, but no trace of an oily ammonia compound had been formed. The yield obtained was therefore about 93 per cent. of the theoretical.

The obvious conclusion to be drawn from these facts is that crude ethyl diacetyladipate contains two structurally isomeric substances, one of which gives a crystalline, the other an oily diimido-, compound. It has not as yet been possible to prove this supposition, but further experiments on the subject are in progress.

Action of Phenylhydrazine on Ethyl Diacetyladipate.

Ethyl diacetyladipate reacts very readily with phenylhydrazine, giving rise to well-characterised products, the formation of which proves beyond doubt that this substance really has the constitution assigned to it in this paper.

If equal volumes of crude ethyl diacetyladipate and phenylhydrazine are mixed together, a considerable rise of temperature takes place, and in a short time the mixture becomes cloudy, owing to the separation of water. This product, when heated on a water-bath, soon separates into two layers, and on prolonged heating, the whole solidifies to a crystalline cake. In order to purify this crude substance, the mass is first ground up in a mortar with ether, filtered from the dark-brown ethereal solution, the residue washed with ether till colourless, and then dried by spreading it on a porous plate. The colourless crystalline mass thus obtained is a mixture of two substances, one of which is soluble in methyl alcohol, the other insoluble.

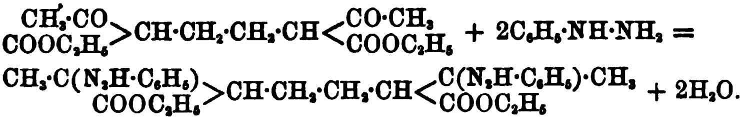
In order to separate these, the crystalline powder is extracted two or three times with boiling methyl alcohol, filtered, and the solution concentrated and allowed to stand. In a short time ethyl diphenylhydrazinediacetyladipate separates in faintly yellowish plates, which after drying first on a porous plate and then over sulphuric acid in a vacuum, gave the following results on analysis.

I. 0·2191 gram substance gave 0·5374 gram CO_2 and 0·1480 gram H_2O.

II. 0·1615 gram substance gave 18 c.c. N; $t = 20°$; bar. = 720 mm.

	Theory.		Found.		
	$C_{26}H_{34}N_4O_4$.		I.	II.	
C......	66·95	per cent.	66·89	—	per cent.
H......	7·30	„	7·50	—	„
N.......	12·02	„	—	12·06	„

This substance is formed by the union of 1 mol. of ethyl diacetyladipate with 2 mols. of phenylhydrazine, with elimination of 2 mols. H_2O, thus:—



$$\begin{array}{l}CH_3\cdot CO\\COOC_2H_5\end{array}\!>\!CH\cdot CH_2\cdot CH_2\cdot CH\!<\!\begin{array}{l}CO\cdot CH_3\\COOC_2H_5\end{array} + 2C_6H_5\cdot NH\cdot NH_2 =$$

$$\begin{array}{r}CH_3\cdot C(N_2H\cdot C_6H_5)\\COOC_2H_5\end{array}\!>\!CH\cdot CH_2\cdot CH_2\cdot CH\!<\!\begin{array}{l}C(N_2H\cdot C_6H_5)\cdot CH_3\\COOC_2H_5\end{array} + 2H_2O.$$

Ethyl diphenylhydrazinediacetyladipate melts at about 143—145°, but when heated above this point decomposition sets in very rapidly; at

200°, the mass again becomes solid, owing to its conversion into bisphenylmethylmethylenepyrazolone (see below).

It is readily soluble in strong acids, but insoluble in alkalis. It dissolves moderately easily in boiling methyl alcohol, but only very sparingly in ether, toluene, ethyl acetate, chloroform, acetone, or light petroleum in the cold. From its solution in hot methyl or ethyl alcohol, it crystallises on slowly cooling in thin, colourless four-sided plates or long, slender needles.

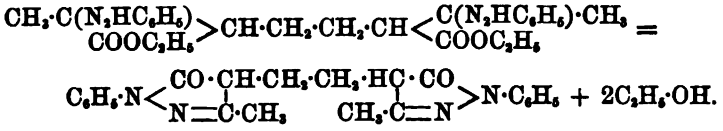
The second substance which is formed when ethyl diacetyladipate and phenyhyldrazine react, and which remains as a white powder after extracting the ethyl diphenylhydrazinediacetyladipate by boiling methyl alcohol as described above, is best purified by recrystallisation from dilute acetic acid. For this purpose the substance is dissolved in boiling acetic acid, the hot liquid filtered, and water added until a very slight turbidity is produced. The solution, on standing, then deposits the new compound in colourless, prismatic crystals, which, after collecting, washing first with dilute acetic acid and then with water, and drying at 130°, gave the following results on analysis:—

I. 0·1537 gram substance gave 0·3960 gram CO_2 and 0·0853 gram H_2O.

II. 0·2830 gram substance gave 37·5 c.c. N; $t = 10°$; bar. = 722 mm.

	Theory. $C_{22}H_{22}N_4O_2$.		Found. I.	Found. II.	
C......	70·58	per cent.	70·26	—	per cent.
H......	5·88	„	6·16	—	„
N......	14·97	„	—	15·06	„

This substance is formed from ethyl diphenylhydrazinediacetyladipate by elimination of two molecules of alcohol, thus:—



$$\begin{array}{r}\mathrm{CH_3\cdot C(N_2HC_6H_5)}\\ \mathrm{COOC_2H_5}\end{array}\!>\mathrm{CH\cdot CH_2\cdot CH_2\cdot CH}<\!\begin{array}{l}\mathrm{C(N_2HC_6H_5)\cdot CH_3}\\ \mathrm{COOC_2H_5}\end{array} =$$

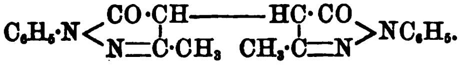
$$\mathrm{C_6H_5\cdot N}<\!\begin{array}{l}\mathrm{CO\cdot CH\cdot CH_2\cdot CH_2\cdot HC\cdot CO}\\ \mathrm{N{=}C\cdot CH_3\quad\ \ CH_3\cdot C{=}N}\end{array}\!>\mathrm{N\cdot C_6H_5} + \mathrm{2C_2H_5\cdot OH}.$$

and is, therefore, bis-1-phenyl-3-methyl-4-methylene-5-pyrazolone. It is almost insoluble in neutral organic solvents, but readily soluble in acetic acid. From dilute acetic acid it separates in colourless, prismatic crystals, which do not melt at 250°.

This pyrazolone is readily soluble both in acids and alkalis. If the pure substance be warmed with moderately dilute hydrochloric acid, it dissolves readily, forming a colourless solution, which on cooling deposits the salt, either as a gelatinous mass or in the form of microscopic needles, according to whether the solution was strong or weak. The gelatinous precipitate, on rubbing or warming gently, at once becomes crystalline. On boiling the hydrochloric solution with either ferric or platinic chlorides, a white, sparingly soluble crystalline substance is precipitated, which is possibly an oxidation-product. Warm dilute sulphuric acid also dissolves the pyrazolone readily; on cooling the solution sets to a transparent jelly, which, on rubbing, eventually becomes crystalline, although not so readily as the hydrochloride. A delicate test, which seems to show the presence of very small quantities of this substance, is the following:—A trace of the pyrazolone is gently boiled with concentrated nitric acid, until the oxidation, which sets in at once, is complete (after about two minutes). The resulting, almost colourless solution, on the addition of a few drops of water, deposits a yellow, crystalline substance, which dissolves in potassium hydrate, forming an intensely reddish-brown liquid.

Bis-phenylmethylmethylenepyrazolone combines very readily with alkalis. The potassium salt was obtained as follows:—The substance was dissolved in a little warm potassium hydrate (sp. gr. 1·2), and then mixed with a concentrated solution of the alkali (sp. gr. 1·4), until a decided precipitate was obtained. This dissolved on boiling, and on allowing the solution to cool slowly, the potassium salt crystallised out in large, transparent, flaky crystals. These were collected, washed four or five times with small quantities of water, and freed from mother liquor as completely as possible by spreading on a porous plate. The resulting satiny crystals dissolved in water very readily, producing a faintly alkaline solution, which showed the following behaviour with precipitants:—*Copper sulphate.*—A pinkish-white precipitate, very sparingly soluble even in boiling water. *Cadmium chloride.*—A heavy white, crystalline precipitate, very sparingly soluble in water. *Silver nitrate.*—A white, gelatinous precipitate, which on boiling turned black. *Uranium nitrate.*—An orange-white precipitate, resembling ferric benzoate in appearance.

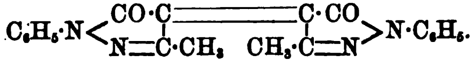
From the study of these properties it is at once evident that a great similarity exists between this substance and bis-phenylmethylpyrazolone:—



$$C_6H_5\cdot N\left\langle\begin{matrix}CO\cdot CH\text{———}HC\cdot CO\\ N{=}C\cdot CH_3\quad CH_3\cdot C{=}N\end{matrix}\right\rangle NC_6H_5.$$

which Knorr (*Ber.*, **17**, 2050) obtained by the action of phenylhydrazine on ethyl diacetylsuccinate.

There is, however, one characteristic difference between these two substances, bis-phenylmethylpyrazolone on oxidation with ferric or platinic chlorides yields pyrazole-blue:—



$$C_6H_5\cdot N<\begin{matrix}CO\cdot C = = = = C\cdot CO \\ N=C\cdot CH_3 \quad CH_3\cdot C=N\end{matrix}>N\cdot C_6H_5.$$

Knorr, (*Annalen*, **238**, 171), whilst bis-phenylmethylmethylenepyrazolone, as might be expected from an examination of its constitution, yields no trace of colouring matter when subjected to similar treatment.

If, however, a solution of the substance in dilute hydrochloric acid is boiled with excess of ferric chloride, a crystalline precipitate is soon produced; this is deposited from its solution in hot dilute acetic acid as a sandy crystalline mass, insoluble in alkalis. It was not analysed.

DECOMPOSITION OF ETHYL DIACETYLADIPATE BY HEAT.

In studying this interesting decomposition, crude ethyl diacetyladipate in quantities of 15 grams at a time, was first submitted to rapid distillation under reduced pressure (225 mm.) from retorts not fitted with thermometers. A large quantity of a slightly yellowish oil distilled over, leaving a considerable carbonaceous residue in the retorts. The distillation from several such operations was next very carefully fractioned under 225 mm. pressure. Below 180° a small quantity of ethyl acetyltrimethylenecarboxylate passed over; then the thermometer rose rapidly to 200°, between which temperature and 240° the greater part distilled as a yellowish oil, leaving a small residue in the retort which was not further examined.

On repeatedly fractioning this distillate under the same pressure, a considerable quantity of an almost colourless oil was obtained, which boiled fairly constantly at 230—231°. This oil on analysis gave the following numbers, each analysis being made from a different preparation.

I. 0·2165 gram substance gave 0·5013 gram CO_2 and 0·1553 gram H_2O.

II. 0·1947 gram substance gave 0·4483 gram CO_2 and 0·1342 gram H_2O.

III. 0·1522 gram substance gave 0·3504 gram CO_2 and 0·1092 gram H_2O.

IV. 0·1669 gram substance gave 0·3859 gram CO_2 and 0·1164 gram H_2O.

	Theory for $C_{14}H_{20}O_5$.	Found. I.	II.	III.	IV.
C.......	62·68 p. c.	63·15	62·74	62·79	63·03 p. c.
H.......	7·47 „	7·96	7·66	7·97	7·74 „
O.......	29·84 „	28·89	29·60	29·24	29·23 „

From this result the conclusion was at once drawn that the substance is formed simply by the elimination of 1 mol. H_2O from 1 mol. ethyl diacetyladipate, thus:—

$$C_{14}H_{22}O_6 = C_{14}H_{20}O_5 + H_2O.$$

Subsequent experiments showed that, in spite of its constant boiling-point, it was a mixture of at least three compounds, and this rendered a very careful reinvestigation of this product very desirable. A large quantity of crude ethyl diacetyladipate which had accumulated as a bye-product from various researches, was submitted to distillation under a pressure of 160 mm. The crude, oily distillate was carefully fractioned, and all passing over between 200—225° (160 mm.) collected apart. This oil, which on analysis gave numbers closely agreeing with those obtained above, was dissolved in five times its bulk of ether, and thoroughly agitated with a small quantity of a moderately dilute solution of potassium hydrate, the aqueous layer was separated, and the operation repeated until the potash solution was coloured slightly yellow only. The alkaline solutions were carefully preserved and investigated in the way to be explained later. The ethereal solution was dried over anhydrous potassium carbonate, the ether distilled off, and the resulting oily residue submitted to very careful fractionation under a pressure of 170 mm. In this way a slightly yellowish oil was obtained, boiling constantly at 215—217° (170 mm.), which on analysis gave the following numbers:—

I. 0·1549 gram substance gave 0·1170 gram H_2O and 0·3720 gram CO_2

II. 0·1544 gram substance gave 0·1189 gram H_2O and 0·3698 gram CO_2.

	Found. I.	II.
C.............	65·49	65·32 per cent.
H.............	8·39	8·55 „
O.............	26·12	26·13 „

As this operation had evidently removed a considerable quantity of a substance containing a lower percentage of carbon than the principal constituent of the oil, it was thought that if the treatment with potash were repeated, a pure product might be obtained. The oil was therefore again dissolved in ether, and the agitation with potash continued until the alkali apparently had no further action on it.

The product, after two or three fractionations, distilled very constantly at 215—217° (167 mm.), and gave the following numbers on analysis:—

I. 0·1947 gram substance gave 0·1465 gram H_2O and 0·4718 gram CO_2.

II. 0·1710 gram substance gave 0·1250 gram H_2O and 0·4140 gram CO_2.

	Found.		
	I.	II.	
C	66·04	66·02	per cent.
H	8·36	8·12	„
O	25·60	25·86	„

As this result was still considered unsatisfactory, the treatment with potash was twice more repeated, the oil being redistilled between each operation. The resulting, almost colourless oil passed over for the most part at 191—192° (35 mm.). Analysis:—

I. 0·2220 gram substance gave 0·1640 gram H_2O and 0·5450 gram CO_2.

II. 0·1919 gram substance gave 0·1433 gram H_2O and 0·4730 gram CO_2.

III. 0·1756 gram substance gave 0·1285 gram H_2O and 0·4320 gram CO_2.

	Theory.	Found.			
	$C_{11}H_{16}O_3$.	I.	II.	III.	
C	67·34	66·95	67·22	67·09	p. c.
H	8·16	8·20	8·29	8·13	„
O	24·49	24·85	24·59	24·78	„

Further treatment with potash had practically no effect on the ethereal solution of this substance, as the product boiled at the same temperature, and gave on analysis C = 67·28, H = 8·21.

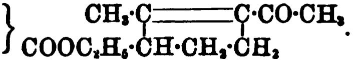
In order to test further the composition of this oil, its molecular weight was determined in acetic acid solution by Raoult's method with the following result:—

Weight of substance	1·2680	grams.
Weight of acetic acid	51·07	„
M. p. of acetic acid	14·76°	
M. p. of mixture	14·27°	
Depression of m. p.	0·49°	

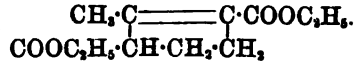
Mol. wt. $C_{11}H_{16}O_3$.	Found.
196	197

Although this substance boils so constantly, it is evident from the study of its decomposition on hydrolysis (see p. 231) that it must consist of two compounds, having their boiling points either identical or lying very near to one another; the second substance being present in very small quantity only.

I. Ethyl methyldihydropentene-methylketonecarboxylate..



II. Ethyl methyldihydropentene-dicarboxylate............



This oil is almost colourless, has a disagreeable odour, and does not solidify when cooled to 0°. It is almost insoluble in water, but readily soluble in alcohol, ether, and most other organic solvents.

Its alcoholic solution does not give any coloration with ferric chloride, although the crude oil before treatment with potash gives an intense violet coloration.

It next appeared interesting to determine the nature of the substance which had been removed by the alkali in the purification of the oil $C_{11}H_{16}O_3$, as described above.

During this operation, each small amount of potash which was used was at once run into a large bottle containing excess of dilute sulphuric acid, in order that the excess of potash might have no further effect on the dissolved oil. The combined extracts were extracted three times with ether, the ethereal solution washed once with water, dried over calcium chloride, and evaporated; in this way a considerable quantity of a dark-brown oil was obtained, which, in alcoholic solution, gave an intense violet coloration with ferric chloride.

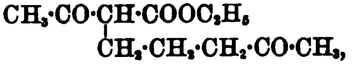
As this oil could not be made to crystallise, it was thought that some idea as to its constitution might be obtained on examining the products formed on distillation under reduced pressure. On gently heating in a fractionation flask (under a pressure of 100 mm.), decomposition rapidly set in with abundant evolution of carbon dioxide, and as the temperature rose a yellow oil distilled without further decomposition. The oily distillate was mixed with ether, extracted twice with dilute potash, to remove acid substances, and then repeatedly fractioned under a pressure of 100 mm. In this way a colourless oil was obtained boiling at 195—200° (100 mm.), which, on analysis, gave the following numbers:—

I. 0·1840 gram substance gave 0·1402 gram H_2O and 0·4150 gram CO_2.

II. 0·1650 gram substance gave 0·1248 gram H_2O and 0 3740 gram CO_2.

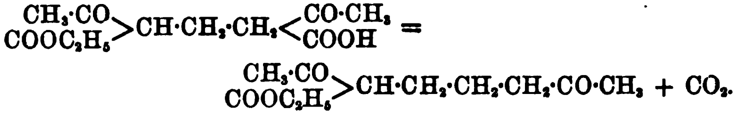
	Theory. $C_{11}H_{18}O_4$.	Found. I.	Found. II.
C	61·68 per cent.	61·45	61·81 per cent.
H	8·41 „	8·47	8·28 „
O	29·90 „	30·08	29·91 „

This new compound is a colourless oil, readily soluble in ether and alcohol, sparingly soluble in water. Its alcoholic solution gives a violet coloration with ferric chloride. A clear insight into the constitution of this oil is obtained from the study of its behaviour on hydrolysis, when it is decomposed into acetovaleric acid, acetic acid, and small quantities of methyldihydropentene methyl ketone (see page 229). This behaviour can only be explained on the assumption that the substance is ethyl *αω*-diacetylvalerate,



$$\begin{array}{l}CH_3{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5\\ \qquad\qquad\;\; |\\ \qquad\qquad CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3,\end{array}$$

a compound which would readily be formed by the distillation of ethyl hydrogen diacetyladipate, thus :—



$$\begin{matrix}CH_3{\cdot}CO\\ COOC_2H_5\end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}CH_2\!<\!\!\begin{matrix}CO{\cdot}CH_3\\ COOH\end{matrix} = \begin{matrix}CH_3{\cdot}CO\\ COOC_2H_5\end{matrix}\!\!>\!CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 + CO_2.$$

The formation of ethyl hydrogen diacetyladipate can be explained on the supposition that the crude product of the distillation of ethyl diacetyladipate still contains some unchanged substance, and that this, on shaking with potash, is partially hydrolysed, and passes into solution as ethyl potassium diacetyladipate.

In order to test this supposition, some crude ethyl diacetyladipate was dissolved in ether and repeatedly agitated with dilute potash solution. The slightly brownish extract was run into dilute sulphuric acid, the resulting turbid solution extracted with ether, and the ethereal solution again agitated with very dilute potash solution. The alkaline liquid, on acidifying, deposited yellowish oily drops, which were extracted with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a considerable quantity of a thick, brownish oil. This oil was completely soluble in sodium carbonate solution; its alcoholic solution gave an intense violet coloration with ferric chloride, and on heating in a small Würtz flask it readily decomposed with evolution of carbon dioxide, and formation of a slightly yellowish, neutral oil, which also gave the violet coloration with ferric chloride. These reactions are exactly similar to those of the oil which was deposited on acidifying the alkaline extract of the product of the distillation of ethyl diacetyladipate, and this experiment tends to strengthen the view of the formation of ethyl diacetylvalerate given above. That the crude substance obtained as described above was in reality ethyl hydrogen diacetyladipate is rendered the more probable by the results of the following analysis of a sample of the crude product, which had been dried over sulphuric acid in a vacuum for 24 hours:—

0·1171 gram substance gave 0·2420 gram CO_2 and 0·0736 gram H_2O.

	Theory. $C_{12}H_{18}O_6$.	Found.
C	55·81 per cent.	56·36 per cent.
H	6·97 ,,	6·99 ,,
O	37·21 ,,	36·65 ,,

HYDROLYSIS OF ETHYL DIACETYLVALERATE.

In studying this decomposition, crude ethyl diacetylvalerate (b. p. 190—210° under 100 mm.) was mixed with an excess of a strong solution of potash in methyl alcohol, and gently boiled on a water-bath in a flask connected with a reflux apparatus. Hydrolysis set in rapidly, the liquid became brownish-coloured, and a quantity of potassium carbonate separated. At the end of two hours the alcohol was distilled off, water added, and the alkaline liquid, which smelt strongly of peppermint, extracted twice with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a small quantity of an oil which smelt strongly of peppermint, and which, on distillation, passed over for the most part between 185° and 200°, and possessed all the properties of methyldihydropentene methyl ketone.

The alkaline solution was evaporated on a water-bath till free from alcohol, mixed with a considerable quantity of water, and acidified with dilute sulphuric acid. The small quantity of a dark-brownish, resinous mass thus precipitated was filtered off, and the clear filtrate extracted repeatedly with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a quantity of a brownish oil which smelt very strongly of acetic acid.

On purifying this by fractionating under reduced pressure (280 mm.), a small quantity of a very acid liquid passed over below 120°, which was readily recognised as acetic acid; then the thermometer rose rapidly to 240°, between which temperature and 260° the greater part distilled. On refractioning, an oil was obtained boiling at 250—253° (280 mm.) which, when cooled in a freezing mixture, solidified to a mass of crystals. These were freed from oily impurities by spreading on a porous plate, remelted, allowed to solidify, again spread on a porous plate, and the colourless crystals thus obtained dried over sulphuric acid, and analysed with the following result:—

0·1792 gram substance gave 0·1378 gram H_2O and 0·3820 gram CO_2.

	Theory. $CH_3 \cdot CO \cdot [CH_2]_4 \cdot COOH$.	Found.
C	58·33 per cent.	58·14 per cent.
H	8·33 ,,	8·54 ,,
O	33·33 ,,	33·32 ,,

Acetovaleric acid thus purified melts at 40—42°, and when heated in small quantities appears to distil at the ordinary pressure without decomposition. It is readily soluble in water, alcohol, ether, and most other organic solvents. Its aqueous solution has a decidedly acid reaction, and gives with phenylhydrazine acetate, after a short time, a precipitate of an oily phenylhydrazine compound.

Acetovaleric acid, which is isomeric with α-ethyl-β-acetopropionic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH(C_2H_5) \cdot COOH$, completes the series of ω-acetocarboxylic acids up to C_9, thus:—

	M. p.
Pyruvic acid, $CH_3 \cdot CO \cdot COOH$..............	Oil
Acetoacetic acid, $CH_3 \cdot CO \cdot CH_2 \cdot COOH$.......	Oil
Levulinic acid, $CH_3 \cdot CO \cdot [CH_2]_2 \cdot COOH$......	33°
ω-Acetobutyric acid, $CH_3 \cdot CO \cdot [CH_2]_3 \cdot COOH$..	Oil
ω-Acetovaleric acid, $CH_3 \cdot CO \cdot [CH_2]_4 \cdot COOH$ ..	40–42°
ω-Acetocaproic acid, $CH_3 \cdot CO \cdot [CH_2]_5 \cdot COOH$.	30°

Salts of Acetovaleric Acid.

The salts of this acid are mostly soluble in water. For the following experiments, an aqueous solution of the acid was exactly neutralised with ammonia, and the resulting solution of the very readily soluble ammonium salt employed. *Silver nitrate* gives a white, crystalline precipitate which dissolves readily in boiling water, and crystallises out on cooling in beautiful, colourless, leafy masses. For analysis, the salt was collected, well washed with water, and dried over sulphuric acid in a vacuum.

I. 0·2516 gram substance gave 0·0980 gram H_2O, 0·3054 gram CO_2, and 0·1082 gram silver.
II. 0·2032 gram substance gave 0·0780 gram H_2O, 0·2476 gram CO_2, and 0·0875 gram silver.
III. 0·2596 gram substance gave 0·1117 gram silver.

	Theory. $C_7H_{11}AgO_3$.	Found. I.	II.	III.	
C......	33·46 p. c.	33·10	33·23	—	p. c.
H......	4·38 „	4·33	4·26	—	„
Ag.....	43·04 „	43·00	43·06	43·02	„

This silver salt is very stable, and not readily affected by light.

Copper sulphate gives no precipitate when mixed with a moderately dilute solution of the ammonium salt. On boiling, however, a greenish-white precipitate separates, which has a crystalline appearance. When examined under the microscope, it was found to consist of a mass of minute, transparent spherules.

HYDROLYSIS OF THE OIL $C_{11}H_{16}O_3$.

In order to obtain some clue as to the constitution of this oil, its behaviour when treated with alcoholic potash was next very carefully investigated.

52 grams of the oil (1 mol.) was dissolved in a little methyl alcohol, heated to boiling in a flask connected with a reflux apparatus, and a solution of 40 grams of pure potash (4 mols.) in methyl alcohol run in drop by drop. During this operation, which occupied about half-an hour, the solution became brownish and deposited a quantity of potassium carbonate; as soon as all the potash solution had been run in, the alcohol was quickly distilled off, and the dark-coloured oil which was precipitated on the addition of water extracted three times with ether. The ethereal solution, after well washing with water, drying over potassium carbonate, and evaporating, deposited 19 grams of a dark-coloured oil, which, on fractionating, distilled for the most part between 180° and 210°, leaving, however, a considerable quantity of a thick, oily residue of high boiling point in the retort. After repeated fractioning in a Würtz flask, provided with a long neck, 8 grams of oil were obtained boiling constantly at 191—191·5° (Analysis I).

Analyses II and III were made with a different preparation which boiled at 188—190° (720 mm.).

I. 0·1680 gram substance gave 0·1473 gram H_2O and 0·4771 gram CO_2.

II. 0·1868 gram substance gave 0·1665 gram H_2O and 0·5293 gram CO_2.

III. 0·1668 gram substance gave 0·1458 gram H_2O and 0·4709 gram CO_2.

	Theory. $C_8H_{12}O$.	Found. I.	II.	III.
C......	77·42 p. c.	77·39	77·22	76·91 p. c.
H......	9·68 „	9·74	9·90	9·72 „
O......	12·90 „	12·87	12·88	13·37 „

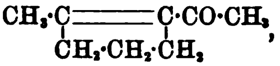
This substance is a colourless, very volatile oil, possessing a penetrating odour of peppermint. It is readily soluble in most organic solvents, insoluble in and lighter than water. It combines readily with phenylhydrazine and with hydroxylamine, forming in the former case an oily hydrazine compound, in the latter case a beautifully crystalline oxime.

This interesting substance, $C_8H_{12}O$, is identical with the compound produced by the action of dehydrating agents on $\omega\omega_1$-diacetylbutane (see next paper).

$$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3 = C_8H_{12}O + H_2O.$$

When treated with reducing agents, it takes up 4 atoms of hydrogen and is converted into an alcohol, $C_8H_{16}O$, and this on treatment with hydrogen iodide at 250° yields the hydrocarbon C_8H_{16}.

Arguing from these and other decompositions, which have been fully explained in the introduction, it is probable that the constitution of this substance is represented by the formula—



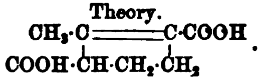
which, according to the nomenclature proposed in the introduction, is the formula of *methyldihydropentene methyl ketone*.

The alkaline liquors obtained in the hydrolysis of the oil, $C_{11}H_{16}O_3$, which had been freed from methyldihydropentene methyl ketone by extraction with ether, as described above, were acidified with dilute sulphuric acid, and extracted 10 times with ether.

The ethereal solution, after washing with small quantities of water till free from alcohol, deposited, on evaporation, about 5 grams of a thick, brown oil, which even after long standing showed no signs of crystallisation. It was, therefore, found necessary to submit this crude product to some process of purification, and after numerous experiments, the following method was found to give the best results. The crude oil was mixed with half a litre of water, heated to boiling, and a hot concentrated solution of barium hydrate added until the liquid had acquired a distinctly alkaline reaction. The excess of baryta was removed by passing a stream of carbon dioxide, the hot solution filtered, and the barium carbonate precipitate, which, owing to its having carried down a quantity of impurity, was distinctly brownish, was well washed with hot water. The filtered solution was acidified with hydrochloric acid, extracted 10 times with ether, the ether evaporated, and the residual oil treated a second time with baryta-water, and again extracted. The resulting yellowish oil was boiled with 1 litre of water, filtered from a little dark coloured insoluble matter, and repeatedly extracted with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited about 12 grams of a yellowish oil; this, on being allowed to remain for some days over sulphuric acid in a vacuum, deposited crystals, but did not entirely solidify.

The crystals were roughly freed from oily mother liquor by means of a vacuum filter, and the yellowish semi-solid mass spread on a porous plate and allowed to stand for two weeks. The resulting, almost colourless, crystalline product was then readily purified by recrystallisation from water, with the aid of a little animal charcoal; in this way, beautiful glittering needles were obtained, which, after drying at 100°, gave the following results, on analysis:—

I. 0·1231 gram substance gave 0·0676 gram H_2O and 0·2560 gram CO_2.
II. 0·1843 gram substance gave 0·0894 gram H_2O and 0·3848 gram CO_2.
III. 0·1540 gram substance gave 0·0845 gram H_2O and 0·3180 gram CO_2.



	Theory.	Found. I.	II.	III.	
C	56·47 p. c.	56·71	56·94	56·31	p. c.
H	5·88 „	6·04	5·39	6·09	„
O	37·65 „	37·25	37·67	37·60	„

Methyldihydropentenedicarboxylic acid melts at 188°. It is readily soluble in hot water, alcohol, and acetone, but only sparingly in cold light petroleum, benzene, carbon bisulphide, and chloroform. This acid usually crystallises from water in long, thin, colourless prisms, but on several occasions thick groups of plates have been obtained which are very different from the needle-shaped crystals. If the needles be dissolved in boiling water, the solution crystallises very rapidly on cooling, whereas the hot solution of the plates takes one or two hours to crystallise. Both forms give the same melting point, and the same results on analysis, but I have not yet succeeded in obtaining the needles from the plates or *vice versâ*.

Salts of Methyldihydropentenedicarboxylic Acid.

Ammonium Salt.—In preparing this salt the pure acid was dissolved in a little hot water, the solution rendered slightly alkaline by the addition of ammonia, and allowed to cool over sulphuric acid in a vacuum. This salt is extremely soluble in water, and if the solution is allowed to evaporate over sulphuric acid, a gelatinous residue is obtained.

Normal Silver Salt, $C_8H_8O_4Ag_2$.—If silver nitrate in considerable excess is added to a faintly alkaline solution of the ammonium salt, a heavy white precipitate of the normal silver salt is thrown down. This was collected, washed with a little warm water, and dried over sulphuric acid in a vacuum. Analysis:—

I. 0·1579 gram substance gave 0·0355 gram H_2O and 0·1450 gram CO_2.

I*a*. 0·1438 gram substance gave 0·0801 gram Ag.

	Theory. $C_8H_8O_4Ag_2$.	Found.
C........	25·00 per cent.	24·89 per cent.
H........	2·09 ,,	2·49 ,,
Ag.......	56·25 ,,	55·70 ,,

This salt darkens very readily when exposed to light. When heated it decomposes all at once, giving a very voluminous mass of carbon and silver.

Hydrogen Silver Salt, $C_8H_9O_4Ag$.—In preparing a quantity of the normal silver salt for some experiments, the mother liquors on standing deposited a considerable crop of fine needles. These were collected, washed with a little water, dried over sulphuric acid, and analysed with the following results:—

0·2001 gram substance gave 0·0594 gram H_2O, 0·254 gram CO_2, and 0·0798 gram Ag.

	Theory. $C_8H_9O_4Ag$.	Found.
C........	34·66 per cent.	34·22 per cent.
H........	3·25 ,,	3·29 ,,
Ag.......	38·99 ,,	39·88 ,,

This salt is readily soluble in hot water. The solution on cooling deposits a mass of very slender needles. The same salt may be obtained by adding nitrate of silver to a dilute neutral solution of the ammonium salt, filtering off the slight precipitate which forms, and allowing the solution to stand in a dark place; after some time fine needles of the hydrogen silver salt separate. The tendency to form this salt, even in neutral solutions, is so great that it was found extremely difficult to prepare a specimen of normal salt pure enough to give good numbers on analysis, most of the analyses showing a deficiency of 1 to 1·5 per cent. Ag.

A neutral solution of the ammonium salt shows the following behaviour with reagents:—*Copper sulphate* gives a deep, bluish-green precipitate, which is very sparingly soluble even in boiling water. *Lead acetate* gives only a slight precipitate in the cold; on warming, the solution becomes turbid and a white amorphous salt separates, which, however, dissolves again on cooling. *Cadmium chloride* gives no precipitate.

The following experiments were conducted with the small quantity of acid at my disposal.

Action of Bromine on Methyldihydropentenedicarboxylic Acid.

A solution of the pure acid in glacial acetic acid seems not to be acted on by bromine even on warming. If, however, an aqueous solution of the acid is mixed with bromine water, decolorisation takes place in the cold. On evaporating the solution, a syrupy residue is obtained, which when warmed, rapidly turns black and gives off hydrogen bromide. It was also found that when the acid was first converted into the chloride by means of PCl_5, and then treated with bromine (as recommended by Baeyer (*Annalen*, **245**, 162), that addition took place at once; but, in spite of several attempts, the dibrominated acid could not be obtained in the crystalline condition.

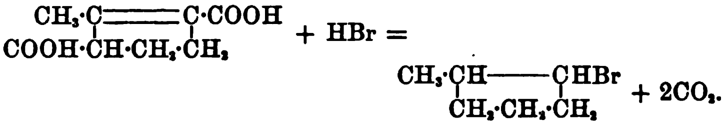
Action of Hydrobromic Acid on the Acid.

Two grams of the pure acid were heated with 14 c.c. of hydrobromic acid (sp. gr. 1·65) in a sealed tube for 4 hours at 100° and then for 3 hours at 120°. On opening the tube much carbon dioxide escaped, and the product on examination was found to consist of an almost colourless liquid in which light-brown, oily drops were suspended. The whole was extracted with ether, the ethereal solution rapidly washed, dried over calcium chloride, and the ether evaporated. The residual, light-brown oil, which weighed 1·3 gram, was placed over sulphuric acid in a vacuum, and then analysed with the following result:—

0·1907 gram substance, heated at 180° for 4 hours with fuming nitric acid, gave on precipitation with $AgNO_3$, 0·2164 gram AgBr.

	Theory. $C_6H_{11}Br$.	Found.
Br........	49·08 per cent.	48·22 per cent.

It is extremely probable that this substance is methylbromopentamethylene, formed according to the equation—



$$\begin{array}{l} CH_3\cdot C=\!=\!=\!=C\cdot COOH \\ COOH\cdot CH\cdot CH_2\cdot CH_2 \end{array} + HBr = \begin{array}{l} CH_3\cdot CH——CHBr \\ CH_2\cdot CH_2\cdot CH_2 \end{array} + 2CO_2.$$

The substance was a brownish oil, having an odour somewhat resembling that of trimethylene bromide. On standing, it became darker and darker, and ultimately almost black, considerable quantities of hydrogen bromide being evolved.

Action of Sodium Amalgam on the Acid.

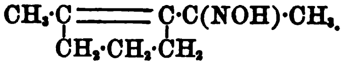
Two grams of the pure acid were dissolved in a little sodium carbonate, and gradually mixed with 250 grams of 3 per cent. sodium amalgam. The product was filtered, acidified with sulphuric acid, the precipitate collected, and recrystallised from water. In this way beautiful colourless needles were obtained which melted at 188°, and possessed all the properties of the original acid. The analysis showed that no addition of hydrogen had taken place:—

0·1446 gram substance gave 0·0762 gram H_2O and 0·2996 gram CO_2.

	Theory. $C_8H_{10}O_4$.	Found.
C	56·47 per cent.	56·57 per cent.
H	5·88 "	5·85 "
O	37·65 "	37·58 "

Further experiments on the action of reducing agents on this acid are in progress.

METHYLDIHYDROPENTENEMETHYLKETONEOXIME.



$$\begin{array}{l} CH_3\cdot C=\!=\!=\!=C\cdot C(NOH)\cdot CH_3. \\ \quad CH_2\cdot CH_2\cdot CH_2 \end{array}$$

In order to prove the ketonic nature of methyldihydropentene methyl ketone, its behaviour towards hydroxylamine was carefully studied.

Six grams of the pure substance dissolved in a little methyl alcohol was mixed with a solution of 5 grams of hydroxylamine hydrochloride in as little water as possible, and then 12 grams of pure potassium hydrate dissolved in methyl alcohol slowly added. After standing for 24 hours the product was mixed with water, gently evaporated to expel the alcohol, well cooled, and then rendered faintly acid by the addition of dilute hydrochloric acid. A considerable quantity of a white, crystalline precipitate separated, which was collected, well washed with water, dried on a porous plate, and recrystallised from light petroleum. A small quantity of oxime which remains dissolved in the aqueous liquors may be obtained as a thick oil by extracting with ether, drying over calcium chloride, and evaporating. This solidifies for the most part on standing, and may be readily purified by leaving it in contact with a porous plate till free from oily mother liquor, and then recrystallising from light petroleum. Analysis:—

0·1301 gram substance gave 0·3290 gram CO_2 and 0·1118 gram H_2O.

0·1210 gram substance gave 10·5 c.c. N; bar. = 759; t = 14°.

	Theory. $C_8H_{13}NO$.	Found.
C	69·06 per cent.	68·96 per cent.
H	9·36 „	9·54 „
N	10·07 „	10·31 „

Methyldihydropentenemethylketoneoxime crystallises from light petroleum in thick, colourless prisms which melt at 85°. It is readily soluble in alcohol, ether, and most other organic solvents, also in acids and alkalis.

Heated in small quantities in a test tube, it distils with only slight decomposition as a colourless oil, which on cooling solidifies completely.

Action of Beckmann's Mixture on Methyldihydropentenemethylketoneoxime.

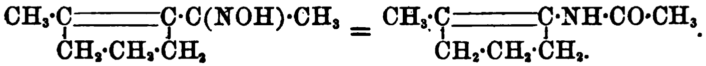
The following experiments were instituted with the object of proving the presence of an acetyl-group in methyldihydropentene methyl ketone.

E. Beckmann, in his interesting researches on intermolecular change in oximes, has shown that methylketoneoximes under the influence of various reagents, such as phosphorus pentachloride, concentrated sulphuric acid, acetyl chloride, and especially a mixture of acetic acid and anhydride saturated with hydrogen chloride, are converted into substituted acetamides, and these when submitted to hydrolysis yield acetic acid and the corresponding primary amine, thus:—

$$R{\cdot}C(NOH){\cdot}CH_3 = RNH{\cdot}CO{\cdot}CH_3$$
$$RNH{\cdot}CO{\cdot}CH_3 + H_2O = RNH_2 + COOH{\cdot}CH_3.$$

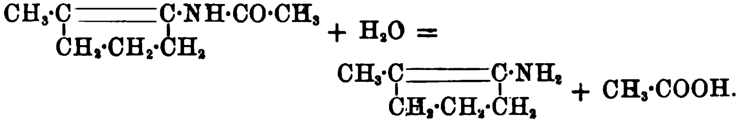
Acetophenoneoxime under these conditions yields acetanilide, whilst methylpropylketoneoxime, $C_3H_7{\cdot}(CH_3)C{:}NOH$, is converted into propylacetamide, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_3H_7$, which then on hydrolysis yield acetic acid and aniline, or propylamine respectively. This reaction may therefore be very widely employed in determining the composition of ketones.

Methyldihydropentenemethylketoneoxime, under like treatment, might be expected to yield in the first place methyldihydropenteneacetamide:—



$$\begin{array}{l} CH_3{\cdot}C{=\!=\!=\!=}C{\cdot}C(NOH){\cdot}CH_3 \\ \quad CH_2{\cdot}CH_2{\cdot}CH_2 \end{array} = \begin{array}{l} CH_3{\cdot}C{=\!=\!=\!=}C{\cdot}NH{\cdot}CO{\cdot}CH_3 \\ \quad CH_2{\cdot}CH_2{\cdot}CH_2. \end{array}$$

which on hydrolysis would then yield methyldihydropenteneamine, and acetic acid:—



$$\begin{array}{l} CH_3{\cdot}C{=\!=\!=\!=}C{\cdot}NH{\cdot}CO{\cdot}CH_3 \\ \quad CH_2{\cdot}CH_2{\cdot}CH_2 \end{array} + H_2O = \begin{array}{l} CH_3{\cdot}C{=\!=\!=\!=}C{\cdot}NH_2 \\ \quad CH_2{\cdot}CH_2{\cdot}CH_2 \end{array} + CH_3{\cdot}COOH.$$

In order to test this, 9 grams of the oxime was dissolved in 90 grams of glacial acetic acid, 20 grams of acetic anhydride added, and the mixture saturated with hydrogen chloride, care being taken that the temperature remained below 30° during the operation. The reddish-brown solution thus obtained was heated in four sealed tubes at 100° for two hours, the resulting, bluish-black liquid transferred to a beaker, mixed with an equal bulk of water, and rendered distinctly alkaline by the addition of sodium hydrate. The dark-coloured product, which contained a quantity of a black tarry mass in suspension, was extracted ten times with ether, the ether distilled off, and the residual, dark-brown oil submitted to rapid distillation in a current of steam. The strongly alkaline distillate, containing a minute quantity of oil in suspension, was acidified with hydrochloric acid, extracted twice with ether, rendered alkaline again, saturated with anhydrous potassium carbonate, and the basic substance which was precipited as an oil extracted by agitating ten times with pure ether. The ethereal solution was dried over freshly ignited potassium carbonate, filtered, and the resulting colourless oil carefully fractioned, when the whole passed over between 160 and 170°.

After repeated fractionation over freshly ignited barium oxide, the new substance was readily obtained pure, boiling constantly at 164—165°. The analysis gave the following results:—

I. 0·1548 gram substance gave 0·3899 gram CO_2 and 0·1332 gram H_2O.

II. 0·1921 gram substance gave 0·4820 gram CO_2 and 0·1621 gram H_2O.

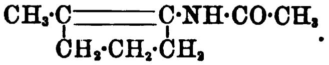
Ia. 0·1317 gram substance gave 12 c.c. N; bar. = 740 mm.; $t = 18$.
IIa. 0·1267 gram substance gave 10·8 c.c. N; bar. = 741 mm.; $t = 18$.
III. 0·1626 gram substance gave 14·5 c.c. N; bar = 740 mm.; $t = 17$.

	Theory. $C_8H_{13}NO$.	Found. I.	II.	III.	
C	69·06 p. c.	68·79	68·90	—	p. c.
H	9·36 „	9·55	9·37	—	„
N	10·07 „	10·45	10·05	10·25	„

This substance, $C_8H_{13}NO$, is a colourless oil possessing a very pungent and disagreeable odour, closely resembling that of pentamethylenediamine.

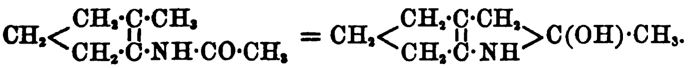
It mixes with water in all proportions with considerable evolution of heat, and it is also soluble in most organic solvents. With acids, it forms readily soluble salts; the platinochloride, which will be described further on, crystallises from water in magnificent, orange-red prisms.

This base is isomeric with methyldihydropentenemethylketoneoxime, and had the reaction proceeded normally, it should have the constitution—



$$\begin{array}{l}CH_3{\cdot}C{=\!=\!=}C{\cdot}NH{\cdot}CO{\cdot}CH_3\\ \quad\ CH_2{\cdot}CH_2{\cdot}CH_2\end{array}.$$

From its method of purification, and especially on account of its powerful basic properties, it is very evident that this formula cannot possibly represent its constitution. Such a substance would on distillation with dilute sodium hydrate be at at once split up, yielding methyldihydropenteneamine and sodium acetate; the amides, moreover, have but very feeble basic properties; they are mostly solid substances, and boil at very high temperatures (capronamide, $C_6H_{13}NO$, boils at 255°). It is, however, extremely probable that the first step in the formation of this base is the conversion of the oxime into methyldihydropenteneacetamide—which then undergoes further intermolecular change—being converted into a stable base, containing two 5-rings; the one made up of carbon-atoms only, the other containing four carbon- and one nitrogen-atoms; thus:—



$$CH_2{<}\begin{array}{l}CH_2{\cdot}C{\cdot}CH_3\\ \quad\ \ \|\\ CH_2{\cdot}C{\cdot}NH{\cdot}CO{\cdot}CH_3\end{array} = CH_2{<}\begin{array}{l}CH_2{\cdot}C{\cdot}CH_2\\ \quad\ \ \|\\ CH_2{\cdot}C{\cdot}NH\end{array}{>}C(OH){\cdot}CH_3.$$

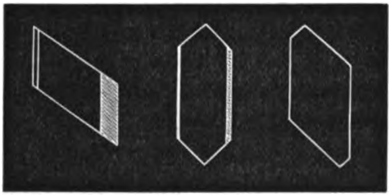
Platinochloride cf $C_8H_{13}NO$.

This magnificent salt is readily obtained by mixing the moderately concentrated solution of the base in hydrochloric acid with an excess of platinum chloride. The solution usually remains clear for some time, but on standing beautiful, orange-coloured tufts of crystals appear. After 24 hours these were collected, washed with water, recrystallised from this solvent, and analysed with the following results:—

I. 2081 gram substance gave 0·0788 gram H_2O, 0·2140 gram CO_2, and 0·0586 gram Pt.
Ia. 0·1479 gram substance gave 4·3 c.c. N; $t = 15°$; bar. = 750 mm.
II. 0·2957 gram substance gave 0·0839 gram Pt.
III. 0·1129 gram substance gave 0·0320 gram Pt.

	Theory. $(C_8H_{13}NO)_2H_2PtCl_6$.		Found. I.	Found. II.	Found. III.	
C........	27·95	p. c.	28·04	—	—	p. c.
H......	4·08	,,	4·20	—	—	,,
N......	4·08	,,	4·32	—	—	,,
Pt......	28·24	,,	28·16	28·38	28·35	,,

This salt is very readily soluble in hot water, moderately soluble in cold. The strong solution in hot water, which has a deep orange-red colour, deposits the salt on cooling in magnificent, red crystals, of the following forms:—



The crystals dissolve readily in boiling absolute alcohol, forming a light-yellow solution; on cooling, the substance crystallises out in long, thin, pale-yellow needles.

When heated in a tube, the dry substance decomposes rapidly at 190—193°, turning perfectly black and giving off a quantity of gas.

Heriot Watt College,
Edinburgh.

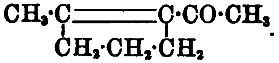
XV.—*$\omega\omega_1$-Diacetylbutane.*

By T. Rhymer Marshall, D.Sc., and W. H. Perkin, Jun., Ph.D.

This paper which is a continuation of the preceding one, contains a description of the preparation and properties of the following substances :—

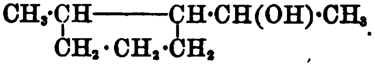
$\omega\omega_1$-Diacetylbutane ... $CH_3\cdot CO\cdot[CH_2]_4\cdot CO\cdot CH_3$.

Methyldihydropentene-methyl ketone......



$$\begin{array}{l} CH_3\cdot C = C\cdot CO\cdot CH_3 \\ \quad\; CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

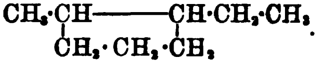
Methylpentamethylene-methyl carbinol ....



$$\begin{array}{l} CH_3\cdot CH - CH\cdot CH(OH)\cdot CH_3 \\ \quad\; CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

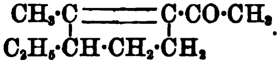
together with the iodide and acetate of this alcohol.

Methylethylpentamethylene................



$$\begin{array}{l} CH_3\cdot CH - CH\cdot CH_2\cdot CH_3 \\ \quad\; CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

Methylethyldihydropentene methyl ketone..



$$\begin{array}{l} \quad CH_3\cdot C = C\cdot CO\cdot CH_3 \\ C_2H_5\cdot CH\cdot CH_2\cdot CH_2 \end{array}.$$

and also of numerous other substances obtained as bye-products, in the preparation of the above compounds.

$\omega\omega_1$-Diacetylbutane, $CH_3\cdot CO[CH_2]_4\cdot CO\cdot CH_3$.

Owing to the ease with which diacetylbutane is converted into methyldihydropentene methyl ketone, it has been found extremely difficult to prepare this substance in a pure state. The following method has, however, on two or three occasions been used with success.

Five grams of pure ethyl diacetyladipate (prepared from the ammonium compound, p. 219) were dissolved in a little methyl alcohol, mixed with a slight excess of a strong solution of pure potash in methyl alcohol, and heated to boiling on a water-bath for 15 minutes. The alcoholic solution was filtered from the precipitated potassium carbonate, the filtrate mixed with twice its volume of water, neutralized with dilute sulphuric acid, and the alcohol distilled off. The residue was extracted three times with ether, the ethereal solution washed with water, dried over anhydrous potassium carbonate, and evaporated. The resulting, almost colourless oil, after standing over sulphuric acid in a vacuum for some days in a cold place, deposited a quantity of flaky crystals, and in one case solidified almost entirely.

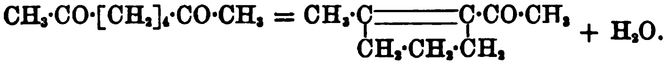
These crystals were freed from oily impurities by spreading on a porous plate, and in this way a beautiful, colourless, flaky, crystalline mass was obtained, which on analysis gave the following numbers:—

0·1380 gram substance gave 0·1220 gram H_2O and 0·3410 gram CO_2.

	Theory. $CH_3\cdot CO\cdot[CH_2]_4\cdot CO\cdot CH_3$.	Found.
C........	67·60 per cent.	67·39 per cent.
H........	9·86 „	9·82 „
O........	22·54 „	22·79 „

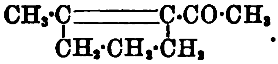
Diacetylbutane is a colourless, crystalline substance which, when purified as above, melts at about 43—44°. It is readily soluble in almost all organic solvents, sparingly so in water. It combines readily with hydrogen sodium sulphate, with phenylhydrazine, and with hydroxylamine, forming well characterised derivatives, which were not prepared in any quantity, or analysed owing to the difficulty experienced in obtaining sufficient pure diacetylbutane.

Under the influence of dehydrating agents, or by simply boiling with alcoholic potash, and apparently also on distillation, diacetylbutane undergoes internal condensation, yielding methyldihydropentene methyl ketone.



$$CH_3\cdot CO\cdot[CH_2]_4\cdot CO\cdot CH_3 = \begin{array}{l}CH_3\cdot C=\!=\!=\!=C\cdot CO\cdot CH_3\\ \qquad CH_2\cdot CH_2\cdot CH_2\end{array} + H_2O.$$

Methyldihydropentene methyl ketone,



$$\begin{array}{l}CH_3\cdot C=\!=\!=\!=C\cdot CO\cdot CH_3\\ \qquad CH_2\cdot CH_2\cdot CH_2\end{array}.$$

This substance is readily obtained by the action of strong boiling alcoholic potash on ethyl diacetyladipate. For this purpose it is not necessary to use pure ethyl diacetyladipate; the crude oil which is obtained on distilling the product of the action of ethylene bromide on ethyl sodioacetoacetate with steam, as described in the previous paper, answers equally well.

The quantities most conveniently employed are the following:—

Crude ethyl diacetyladipate, 50 grams.
Caustic potash, 50—55 grams (dissolved in the smallest quantity of boiling 80 per cent. alcohol).

The ethyl diacetyladipate is dissolved in an equal bulk of alcohol, heated to boiling on a water-bath, in a flask connected with a reflux apparatus, and one-third of the potash solution run in. After boiling vigorously for five minutes, another third of the potash solution is added, the mixture boiled for ten minutes, then the remaining potash solution added, and the alcohol at once distilled off. The dark-brown product is mixed with sufficient water to dissolve the potassium carbonate and other potash salts, extracted five times with ether, the ethereal solution washed with water, dried over anhydrous potassium carbonate, and evaporated. In this way a yellowish oil is obtained which should weigh 15 to 20 grams. On distillation, almost the whole of it passes over between 185 and 200° as a colourless oil, leaving only a very small dark residue in the retort, and on refractioning once or twice, the substance is readily obtained pure, and boiling constantly at 191° (760 mm.).

The numbers obtained on analysis agree with those required by the formula $C_8H_{12}O$.

0·1344 gram substance gave 0·1194 gram H_2O and 0·3804 gram CO_2.

	Theory. $C_8H_{12}O$.	Found.
C........	77·42 per cent.	77·19 per cent.
H........	9·68 ,,	9·87 ,,
O........	12·90 ,,	12·94 ,,

Methyldihydropentene methyl ketone, which, by this method, may be obtained in a state of great purity with comparatively little labour, is a colourless, mobile oil, possessing a most powerful odour of peppermint.

A series of carefully conducted experiments have shown that it is identical with the compound obtained by the hydrolysis of the crude product of the distillation of ethyl diacetyladipate, as described in the foregoing paper (p. 231). Both these substances boil at the same temperature; they possess the same odour, have the same specific gravity, and give the same products on reduction.

As it was very important to be certain of the identity of the two substances, the oxime of the product obtained as above was prepared and compared with that previously obtained from the other compound, $C_8H_{12}O$ (p. 232); 1 gram of the pure substance was dissolved in methyl alcohol, mixed with a dilute methyl alcoholic solution of 0·7 gram of hydroxylamine hydrochloride and 1·5 gram of potash, and the whole allowed to stand 24 hours. The resulting, colourless solution was mixed with an equal volume of water, boiled to expel the alcohol, cooled well, and acidified with dilute sulphuric acid. The crystalline precipitate thus obtained was collected, well washed with water, dried on a porous plate, and recrystallised from light petroleum. The beautifully crystalline substance thus obtained gave the following numbers on analysis:—

I. 0·1733 gram substance gave 0·1490 gram H_2O and 0·4395 gram CO_2.

II. 0·2677 gram substance gave 23·8 c.c. N; $t = 14°$; bar. = 744.

	Theory. $C_8H_{13}NO$.	Found.
C........	69·06 per cent.	69·16 per cent.
H........	9·36 „	9·54 „
N........	10·07 „	10·30 „

This oxime melts at 85°, is readily soluble in acids and alkalis, and agrees in all its properties with the substance already described in the last paper (p. 237).

As the yield of methyldihydropentene methyl ketone was far from that which should have been obtained theoretically, it was thought that interesting results might be obtained by examining the solution of the potassium salts from which the above ketone had been extracted.

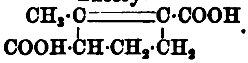
The dark-brown solution was evaporated till free from alcohol, acidified with dilute sulphuric acid, and extracted several times with ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited a dark-brown, acid-smelling oil, which, even after long standing over sulphuric acid in a vacuum, showed no signs of crystallising. In order to purify this crude product, it was dissolved in a slight excess of baryta-water, the solution heated to boiling, and treated with carbon dioxide until the excess of baryta had been removed. On filtering, the solution was found to be much less coloured, whilst the barium carbonate precipitated was distinctly brownish, showing that a considerable quantity of impurity had been removed. The boiling solution of the barium salt was acidified with dilute hydrochloric acid, well agitated, filtered from a small quantity of resinous matter, and after cooling, repeatedly extracted with ether. On drying the ethereal solution over calcium chloride and evaporating, a dark-yellow oil was obtained, which, after standing for some days over sulphuric acid in a vacuum, deposited crystals. These were separated from the oily mother liquor as completely as possible by spreading on a porous plate, and then further purified by recrystallisation from water.

The colourless crystals thus obtained gave the following results on analysis:—

I. 0·2146 gram substance gave 0·1240 gram H_2O and 0·4490 gram CO_2.

II. 0·1594 gram substance gave 0·0903 gram H_2O and 0·3323 gram CO_2.

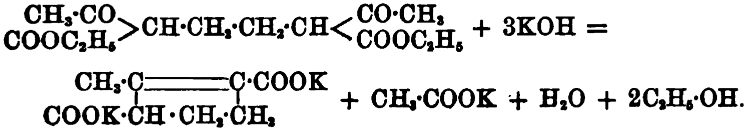
Theory.



$$\begin{array}{l} CH_3\cdot C\!=\!=\!=\!=\!C\cdot COOH \\ COOH\cdot CH\cdot CH_2\cdot CH_2 \end{array}$$

	Theory.	Found. I.	Found. II.
C	56·47 p. c.	56·96	56·86 p. c.
H	5·88 „	6·26	6·29 „
O	37·65 „	36·78	36·85 „

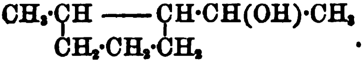
This acid melts at 188°, and is evidently identical with the substance obtained by the hydrolysis of the oil $C_{11}H_{16}O_3$, as described in the last paper. The formation of this acid by the hydrolysis of ethyl diacetyladipate would be represented by the following equation:—



$$\begin{array}{l}CH_3\cdot CO \\ COOC_2H_5\end{array}\!\!>CH\cdot CH_2\cdot CH_2\cdot CH<\!\!\begin{array}{l}CO\cdot CH_3 \\ COOC_2H_5\end{array} + 3KOH =$$

$$\begin{array}{l} CH_3\cdot C\!=\!=\!=\!=\!C\cdot COOK \\ COOK\cdot CH\cdot CH_2\cdot CH_2 \end{array} + CH_3\cdot COOK + H_2O + 2C_2H_5\cdot OH.$$

Action of Reducing Agents on Methyldihydropentene Methyl Ketone. Formation of Methylpentamethylene Methyl Carbinol,



$$\begin{array}{l} CH_3\cdot CH\text{——}CH\cdot CH(OH)\cdot CH_3 \\ \quad CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

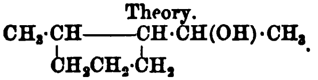
The products obtained in the reduction of methyldihydropentene methyl ketone vary remarkably with the nature of the reducing agents employed; thus, whereas on treatment with sodium in ethereal solution methylpentamethylene methyl carbinol results, when sodium amalgam is employed, scarcely a trace of this substance is formed. In preparing methylpentamethylene methyl carbinol, 20 grams of the ketone was dissolved in 100 grams of ether, the solution floated on about 50 c.c. of water, and about three times the calculated quantity of sodium very gradually added, and if necessary small quantities of water, from time to time, the flask being carefully cooled by a stream of running water. As soon as all the sodium has been added, the ethereal solution was separated, washed with water, dried over potassium carbonate, evaporated, and the resulting, thick, colourless oil submitted to fractional distillation under reduced pressure (55 mm.). In this way the oil was readily separated into two principal fractions, 120—150° and 230—260°. On repeatedly refractioning the lower fraction at ordinary pressures, pure methylpentamethylene methyl carbinol was readily obtained as a colourless oil, boiling constantly at 180°.

Analyses.

I. 0·1231 gram substance gave 0·1412 gram H_2O and 0·3389 gram CO_2.

II. 0·1631 gram substance gave 0·1814 gram H_2O and 0·4487 gram CO_2.

Theory.



$$\begin{array}{l} CH_3\cdot CH\text{———}CH\cdot CH(OH)\cdot CH_3 \\ \quad CH_2CH_2\cdot CH_2 \end{array}$$

	Theory.	Found. I.	Found. II.
C	75·00 p. c.	75·08	75·03 p. c.
H	12·50 „	12·74	12·35 „
O	12·50 „	12·18	12·62 „

Methylpentamethylene methyl carbinol is a colourless, moderately mobile oil, having a strong odour of menthol. It is readily soluble in organic solvents, and also slightly soluble in water.

Methylpentamethylene methyl carbinol yields an acetate when treated with acetic anhydride (p. 249), and an iodide when digested with hydriodic acid (p. 249).

In order to demonstrate the existence of a closed chain in methyl dihydropentene methyl ketone, it was important to show clearly that this substance on reduction is only capable of taking up at the most 4 atoms of hydrogen. As methylpentamethylene methyl carbinol was possibly only an intermediate product of the reduction of the ketone, experiments were made with the view of reducing this alcohol still further.

Five grams of the pure alcohol were mixed with 200 grams of absolute alcohol, heated to boiling on a water-bath, in a flask connected with a reflux apparatus, and then 20 grams of sodium thrown in as rapidly as possible. The product was mixed with water, the alcohol distilled off, and the residue extracted with ether. The resulting oil, on distillation under reduced pressure (80 mm.), distilled at 119—120°, and on subsequent fractioning under ordinary pressure at 178—181°, and gave the following numbers on analysis :—

0·1294 gram substance gave 0·1443 gram H_2O and 0·3532 gram CO_2.

	Theory. $C_8H_{16}O$.	Found.
C	75·00 per cent.	74·44 per cent.
H	12·50 „	12·39 „
O	12·50 „	13·17 „

This result tends to show that methylpentamethylene methyl carbinol is a fully saturated substance, not capable of combining further with hydrogen, a fact which is proved conclusively by the results of the experiments on the action of hydriodic acid on the iodide of this alcohol.

In reducing methyldihydropentene methyl ketone in a moist ethereal solution with sodium, a considerable quantity of a very thick oil is obtained, which boils at about 230—260° (55 mm.). As it was thought that the examination of this substance might lead to interesting results, it was most carefully fractioned several times under a pressure of 50 mm., after which the greater part boiled at 250—255° (50 mm.).

Two separate preparations, both boiling at the same temperature, gave the following results on analysis :—

I. 0·2572 gram substance gave 0·2615 gram H_2O and 0·7230 gram CO_2.

II. 0·1568 gram substance gave 0·1574 gram H_2O and 0·4410 gram CO_2.

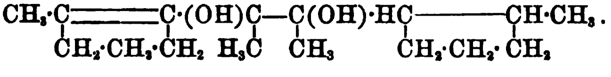
	Theory.	Found.	
	$C_{16}H_{28}O_2$.	I.	II.
C	76·19 p. c.	76·88	76·65 p. c.
H	11·11 ,,	11·29	11·15 ,,
O	12·70 ,,	11·83	12·20 ,,

A determination of its molecular weight by Raoult's method, using acetic acid as a solvent, gave the following results :—

Weight of substance	1·2890
,, acetic acid..................	50·17
Melting point of acetic acid	15·74°
,, mixture...............	15·33
Depression of m. p....................	0·41

Molecular weight, $C_{16}H_{28}O_2$, 252. Found, 244.

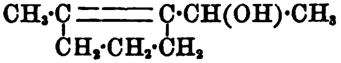
This substance, which appears to have the formula $C_{16}H_{28}O_2$, is a colourless, transparent syrup, so thick that a test-tube half full of the syrup may be inverted for some time without the substance falling out. It has a decided odour of menthol, distils at the ordinary pressure with slight decomposition, and under reduced pressure (50 mm.) at 250—255°, without the slightest decomposition. From its mode of formation and general properties, it appears probable that this substance has the formula—



$$\begin{array}{l} CH_3\cdot C{=}{=}{=}{=}C\cdot(OH)C-C(OH)\cdot HC{-}{-}{-}{-}CH\cdot CH_3 . \\ \quad CH_2\cdot CH_2\cdot CH_2 \quad H_3C \quad CH_3 \qquad CH_2\cdot CH_2\cdot CH_2 \end{array}$$

being a condensation-product derived from 1 mol. of ethyldihydropentene methyl ketone, and 1 mol. of methylpentamethylene methyl ketone.

Reduction of Methyldihydropentene Methyl Ketone by Sodium Amalgam.

During the first experiments on the reduction of this ketone, several attempts were made to obtain the unsaturated alcohol  $\begin{array}{l} CH_3\cdot C = C\cdot CH(OH)\cdot CH_3 \\ \quad CH_2\cdot CH_2\cdot CH_2 \end{array}$ by the action of sodium amalgam on dilute alcoholic solutions of the substance.

The pure ketone was dissolved in 50 per cent. alcohol, and treated with a large excess of 1½ per cent. sodium amalgam, the oil which soon separates out being kept in solution by the addition of further quantities of alcohol. The product of the reaction was a very thick oil, which on fractioning under a pressure of 25 mm. separated into two principal fractions, 220—225° and 250—260°, scarcely a trace of any low boiling substance being obtained.

Fraction 250—260° (25 mm.), which was a very thick, slightly brownish oil, gave on analysis the following numbers:—

0·1800 gram substance gave 0·1703 gram H_2O and 0·5086 gram CO_2.

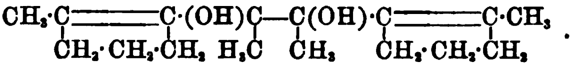
	Theory. $C_{16}H_{26}O_2$.	Found.
C	76·80 per cent.	77·05 per cent.
H	10·40 ,,	10·51 ,,
O	12·80 ,,	12·44 ,,

A determination of its molecular weight by Raoult's method gave the following results:—

Weight of substance............	1·2797 gram.
,, acetic acid	49·14 ,,
Melting point of acetic acid......	15·76°
,, mixture........	15·34°
Depression of melting point.....	0·42°

Molecular weight of $C_{16}H_{26}O_2$, 250. Found, 242.

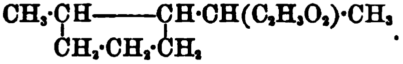
This substance is evidently the pinacone of methyldihydropentene methyl ketone, and its constitution must therefore be represented by the formula—



$$\begin{array}{l} CH_3\cdot C = C\cdot(OH)C - C(OH)\cdot C = C\cdot CH_3 \\ \quad CH_2\cdot CH_2\cdot CH_2 \quad H_3C \quad CH_3 \quad CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

The fraction 220—225° (25 mm.) obtained in the reduction of methyldihydropentene methyl ketone with sodium amalgam gave on analysis numbers agreeing approximately with the formula $C_{16}H_{24}O$ (*i.e.*, $C_{16}H_{26}O_2 - H_2O$), and it is, therefore, probably an anhydride of the above pinacone. As we had only a very small quantity of this substance at our disposal, no further experiments were made with it. It is a very thick, slightly brownish oil, having a faint odour of peppermint.

Methylpentamethylene Methyl Carbinyl Acetate,



$$\begin{array}{l}CH_3\cdot CH\text{——}CH\cdot CH(C_2H_3O_2)\cdot CH_3\\ \quad CH_2\cdot CH_2\cdot CH_2\end{array}.$$

In preparing this substance, the pure alcohol was boiled with twice the calculated quantity of acetic anhydride on a reflux apparatus for two hours, the acetic acid and excess of anhydride distilled off, and the residual oil distilled under reduced pressure.

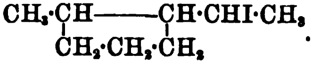
The fraction boiling at 145—150° (130 mm.), gave on analysis the following numbers:—

0·1531 gram substance gave 0·1459 gram H_2O and 0·3960 gram CO_2.

	Theory. $C_{10}H_{18}O_2$.	Found.
C........	70·58 per cent.	70·54 per cent.
H........	10·60 „	10·59 „
O........	18·82 „	18·87 „

This acetate is an agreeably smelling and strongly refracting liquid, which appears to distil under the ordinary pressure without decomposition. In order to more clearly prove its constitution, it was hydrolysed by boiling with excess of standard potash solution for six hours, and the amount of acetate formed determined by estimating the amount of unused alkali present in the solution by means of standard sulphuric acid. It was thus found that 1·349 gram substance on hydrolysis neutralised 79·5 c.c. of standard potash solution, 1 c.c. of which was equal to 0·00597 gram of $CH_3\cdot COOH$. This corresponds to 35·1 per cent. of $CH_3\cdot COOH$, whereas theory requires 35·3 per cent.

Methylpentamethylene Methyl Carbinyl Iodide (Methyl-α-iodethylpentamethylene 1.2),



$$\begin{array}{l}CH_3\cdot CH\text{——}CH\cdot CHI\cdot CH_3\\ \quad CH_2\cdot CH_2\cdot CH_2\end{array}.$$

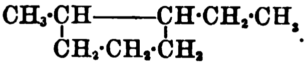
Methylpentamethylene methyl carbinol is readily attacked by boiling hydrochloric, hydrobromic, and hydriodic acids, with formation of heavy oils, consisting no doubt of the corresponding chloride, bromide, and iodide of the alcohol. Of these the latter only has been prepared in quantity and examined. It is best obtained by boiling the alcohol with an excess of hydriodic acid of sp. gr. 1·96 for about half an hour on a reflux apparatus. The product is mixed with twice its volume of water, extracted several times with ether, the ethereal solution washed well with water and dilute sodium carbonate solution, dried over anhydrous potassium carbonate, and evaporated, the resulting oil, after removing free iodine by shaking with mercury, being purified by fractionation under reduced pressure (90 mm.). A considerable portion of the substance distilled between 155 and 160° (90 mm.), and gave on analysis the following numbers:—

0·2543 gram substance heated with nitric acid and nitrate of silver at 180° for four hours gave 0·2460 gram AgI.

	Theory. $C_8H_{15}I$.	Found.
I........	53·21 per cent.	52·26 per cent.

This iodide is a colourless, heavy oil, having an odour strongly resembling that of hexyl iodide. When distilled, even under reduced pressure, it undergoes slight decomposition, with formation of products of high boiling point; it is better for most purposes, therefore, to use the crude oil, without fractioning.

Methylethylpentamethylene (1.2),



$$\begin{array}{l} CH_3\cdot CH\text{———}CH\cdot CH_2\cdot CH_3 \\ \qquad\;\, | \qquad\qquad\;\; | \\ \qquad CH_2\cdot CH_2\cdot CH_2 \end{array}.$$

In preparing this interesting substance, methyl-α-iodethylpentamethylene was heated in sealed tubes with excess of the strongest hydriodic acid and a little amorphous phosphorus at 240—250° for 12 hours. The contents of several tubes, each of which had contained about 5 grams of the iodide, were transferred to a separating funnel, allowed to stand for some hours, and the dark-coloured aqueous liquid separated as completely as possible from the layer of hydrocarbon which floated on the surface. The residual, limpid oil, after drying over potassium carbonate and distilling, passed over completely between 120 and 130°, and after repeated distillation over sodium and lastly over potassium the pure substance was obtained boiling constantly at 124°. The analysis gave the following numbers:—

I. 0·1313 gram substance gave 0·1708 gram H_2O and 0·4136 gram CO_2.

II. 0·1100 gram substance gave 0·1435 gram H_2O and 0·3465 gram CO_2.

	Theory.	Found.	
	C_8H_{16}.	I.	II.
C........	85·71 p. c.	85·91	85·71 p. c.
H........	14·29 „	14·45	14·30 „

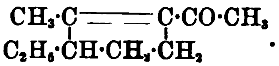
A determination of the vapour-density of this substance, by Victor Meyer's method, in aniline vapour gave the following results:—

0·042 gram substance displaced 8·5 c.c. of air; $t = 13°$ C.; bar. = 755 mm.

Molecular weight calculated, 118. Found, 112.

Methylethylpentamethylene is only with difficulty attacked by bromine; on boiling the two substances together, slight action takes place with evolution of hydrogen bromide. On shaking the hydrocarbon with fuming hydrobromic acid (sp. gr. 1·85) even for days, no appreciable action could be detected. When boiled with nitric acid (sp. gr. 1·16), oxidation rapidly sets in, and in the course of a few hours the oily layer of hydrocarbon entirely disappears and a colourless solution is obtained from which no definite substance could be extracted.

Ethylmethyldihydropentene Methyl Ketone,



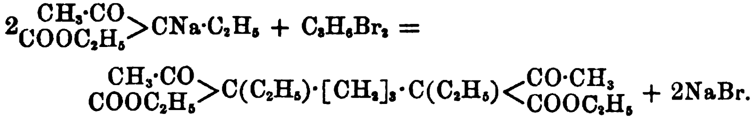
$$\begin{array}{l} CH_3\cdot C\!=\!=\!=\!C\cdot CO\cdot CH_3 \\ C_2H_5\cdot CH\cdot CH_2\cdot CH_2 \end{array}.$$

In order to get some further proof of the constitution of methyldihydropentene methyl ketone, several experiments were made with the object of preparing diethyldiacetylbutane,

$$CH_3\cdot CO\cdot CH(C_2H_5)\cdot CH_2\cdot CH_2\cdot CH(C_2H_5)\cdot CO\cdot CH_3,$$

and studying its behaviour towards dehydrating agents.

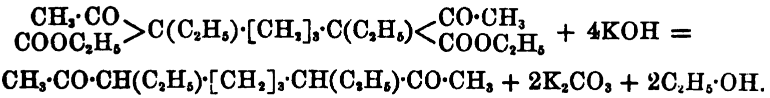
A short time since, Dr. Kipping and one of us (this vol., p. 29 *et seq.*) prepared diethyldiacetylpentane by treating ethylic ethylacetoacetate with sodium ethylate and trimethylene bromide, and hydrolysing the resulting ethylic diethyldiacetylpimelate, thus:—



$$2\genfrac{}{}{0pt}{}{CH_3\cdot CO}{COOC_2H_5}{>}CNa\cdot C_2H_5 + C_3H_6Br_2 =$$

$$\genfrac{}{}{0pt}{}{CH_3\cdot CO}{COOC_2H_5}{>}C(C_2H_5)\cdot[CH_2]_3\cdot C(C_2H_5){<}\genfrac{}{}{0pt}{}{CO\cdot CH_3}{COOC_2H_5} + 2NaBr.$$

Ethyl diethyldiacetylpimelate.



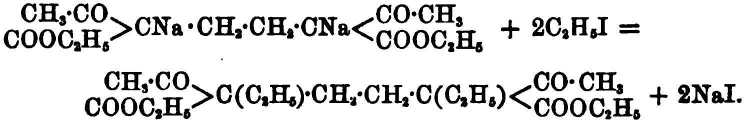
$$\genfrac{}{}{0pt}{}{CH_3\cdot CO}{COOC_2H_5}{>}C(C_2H_5)\cdot[CH_2]_3\cdot C(C_2H_5){<}\genfrac{}{}{0pt}{}{CO\cdot CH_3}{COOC_2H_5} + 4KOH =$$

$$CH_3\cdot CO\cdot CH(C_2H_5)\cdot[CH_2]_3\cdot CH(C_2H_5)\cdot CO\cdot CH_3 + 2K_2CO_3 + 2C_2H_5\cdot OH.$$

Diethyldiacetylpentane.

In endeavouring to prepare diethyldiacetylbutane by substituting ethylene bromide for trimethylene bromide in the above equation, we obtained only a trace of substance of high boiling, which might have been diethyl diacetyladipate, the principal product of the reaction being ethyl butyrate.

We then experimented on the action of ethyl iodide on the disodium compound of ethyl diacetyladipate in the hope of thus obtaining ethylic diethyldiacetyladipate, according to the equation



$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>CNa\cdot CH_2\cdot CH_2\cdot CNa<\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix} + 2C_2H_5I =$$

$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>C(C_2H_5)\cdot CH_2\cdot CH_2\cdot C(C_2H_5)<\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix} + 2NaI.$$

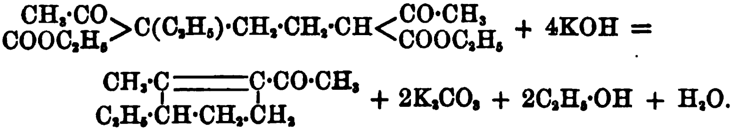
A mixture of 60 grams of crude ethyl diacetyladipate and 60 grams of ethyl iodide were slowly added, with careful cooling, to a solution of sodium ethylate, prepared by dissolving 9·7 grams of sodium in 100 grams of absolute alcohol. The whole was transferred to a soda-water bottle and heated on a water-bath for 12 hours. The alcohol was then distilled off, sufficient water added to dissolve the inorganic salts, and the product extracted four times with ether. The ethereal solution was washed with water, the ether distilled off, and the residual oil at once hydrolysed by boiling with alcoholic potash, the same quantities and the same method of procedure being employed as in the case of ethyl diacetyladipate itself. As soon as hydrolysis was complete the alcohol was distilled off, water added, and the oil which separated repeatedly extracted with ether. The ethereal solution, after washing with water, drying over anhydrous potassium carbonate, and evaporating, deposited a considerable quantity of a brownish oil which, on distillation, all passed over between 200° and 270°. This, on repeated fractionation, separated into two fractions, 210—215° and 250—255°, the latter, however, being very small.

Fraction 210—215° gave the following results on analysis:—

0·1199 gram of substance gave 0·1149 gram H_2O and 0·3375 gram CO_2.

	Theory. $C_{10}H_{16}O$.	Found.
C	78·94 per cent.	78·74 per cent.
H	10·53 „	10·57 „
O	10·53 „	10·69 „

This substance is evidently ethylmethydihydropentene methyl ketone, formed from ethylic ethyldiacetyladipate according to the equation—



$$\begin{matrix}CH_3\cdot CO\\ COOC_2H_5\end{matrix}\!>C(C_2H_5)\cdot CH_2\cdot CH_2\cdot CH<\!\begin{matrix}CO\cdot CH_3\\ COOC_2H_5\end{matrix} + 4KOH =$$

$$\begin{matrix}CH_3\cdot C & = & C\cdot CO\cdot CH_3\\ | & & |\\ C_2H_5\cdot CH\cdot CH_2 & \cdot & CH_2\end{matrix} + 2K_2CO_3 + 2C_2H_5\cdot OH + H_2O.$$

In order to corroborate this, the substance was converted into its oxime. 4 grams of the oil were dissolved in a little methyl alcohol, and mixed with 4 grams of hydroxylamine hydrochloride dissolved in a small quantity of water, and 10 grams of pure potash dissolved in methyl alcohol. After 24 hours, the alcohol was evaporated by gently warming the solution on a water-bath, the residue mixed with water, rendered faintly acid by the addition of a few drops of hydrochloric acid, and repeatedly extracted with pure ether. The ethereal solution, after well washing with water, drying over calcium chloride, and evaporating, deposited the oxime as an oil which showed no signs of crystallisation on standing for 24 hours over sulphuric acid in a vacuum. The analysis gave the following numbers:—

0·1286 gram substance gave 9·4 c.c. N; bar. = 740 m.; t = 13°.

	Theory. $C_{10}H_{17}NO$.	Found.
N	8·38 per cent.	8·40 per cent.

The fraction 250—255° appeared to consist of impure diethyldiacetylbutane, but the quantity obtained was so small that it was found impossible to obtain it in a pure state. With hydroxylamine it gave a solid dioxime.

We hope to be able to prepare this interesting substance by some other reaction, and to study its behaviour with dehydrating agents with a view of proving the formula given in this and the previous paper for methyldihydropentene methyl ketone.

Heriot Watt College,
Edinburgh.

XVI.—*The Action of Chromium Oxychloride on Nitrobenzene.*

By G. G. Henderson, B.Sc., M.A., F.I.C., and J. Morrow Campbell, B.Sc., Donaldson Chemical Scholar, University of Glasgow.

According to Étard (*Ann. Chim. Phys.* [5], **22**, 218), chromium oxychloride attacks nitrobenzene with the formation of a brown, amorphous solid, $C_6H_5(NO_2)(CrO_2Cl)_2$, which, when treated with water, yields chromium chloride and "nitroquinone;" the latter is said to crystallise from hot water, in which it is readily soluble, in shining, yellowish-brown crystals which melt at 232°, and sublime on further heating in brilliant, yellow plates. The same observer states that from nitrotoluene (a mixture of the isomerides), when similarly treated with chromium oxychloride, he obtained "nitrotoluquinone" in the form of yellowish-brown leaves melting at 237°, and with properties resembling those of "nitroquinone." Von Richter, however, showed (*Ber.*, **19**, 1060) that the substance formed by the action of chromium oxychloride on nitrotoluene at about 160° is not a quinone, but is in reality paranitrobenzoic acid; whilst from nitrobenzene he obtained no analogous compound. The action of chromium oxychloride, dissolved in glacial acetic acid, on nitrobenzene was investigated by Carstanjen (*J. pr. Chem.* [N.F.], **2**, 51), who obtained a small quantity of white crystals, which, from preliminary tests, appeared to be trichloronitrobenzoic acid, together with some substance of such exceeding volatility that all attempts to isolate it were unsuccessful. Its vapour was intensely irritating to the eyes, and if a drop of an ethereal solution was allowed to fall on the skin, it caused painful smarting.

Étard's process is the only one by which nitroquinone is said to have been prepared, and it will be seen from what is quoted above that contradictory results have been obtained by other observers. We have, therefore, re-examined the action of chromium oxychloride on nitrobenzene under various conditions in the hope of settling the question one way or another.

Our first experiments were carried out in the way described by Étard, that is, nitrobenzene (carefully purified and dried) was heated to about 160° by means of an oil-bath, and chromium oxychloride was added drop by drop from a tap-funnel. The proportions used were about 1 mol. of nitrobenzene to 2 mols. of the oxychloride, the former being in slight excess. No change was observed until a small quantity of the oxychloride had been added, and then a sudden and very violet action took place, the whole contents of the flask being thrown out in one experiment, and the flask itself broken by the force of the explosion in another. The experiments were repeated under altered conditions, chromium oxychloride being gradually added to nitrobenzene heated to temperatures ranging from 80° to 140°, but the result was always the same, though sometimes we observed the presence of traces of the volatile irritating substance described by Carstanjen.

In the next place, nitrobenzene (1 mol.) and chromium oxychloride (2 mols.) were carefully mixed at the ordinary temperature and left to stand in a flask placed in a vessel of cold water. After some time a sudden and violent action took place, and the flask was broken.

We failed altogether to obtain any "nitroquinone" by any of the experiments described, though they were many times repeated. The only products, besides the volatile substance occasionally formed, were very small quantities of a brown powder, which, on treatment with water, yielded amorphous substances which could not be crystallised, and the analyses of which gave no concordant results.

Another method was therefore adopted. A 50 per cent. solution of chromium oxychloride in pure, dry chloroform was gradually added to a similar solution of nitrobenzene in a flask attached to a reflux condenser. A slow action began, and was accelerated by heating the flask on a water-bath. Fumes of hydrogen chloride were given off and a dark-brown powder slowly separated, though, even after several hours' heating, the reaction was not quite completed. After the precipitate had settled down, the chloroform was poured off, and the precipitate was washed with dry chloroform, quickly transferred to stoppered tubes, and dried at 100°. The brown powder attracts moisture with great avidity, and decomposes almost at once when exposed to the air; it also seems to retain traces of chromium compounds. Analysis gave the following results:—

1·3145 gram substance gave 0·5960 gram Cr_2O_3 and 1·0355 gram AgCl.

	Calculated for $C_6H_3(NO_2)(CrO_2Cl)_2$.	Found.
Cr	29·10 per cent.	31·02 per cent.
Cl	19·66 „	19·47 „

It will be observed that the percentage of chromium found is higher than that demanded by theory, but, as already stated, it is difficult to free the substance entirely from traces of chromium compounds precipitated with it. When thrown into cold water, the compound is decomposed with evolution of much heat and apparently with escape of a gas (possibly oxygen). Chromium chloride and chromic acid are found in solution, while an almost colourless, heavy liquid sinks to the bottom of the flask. This liquid was separated, washed repeatedly, first with dilute caustic soda and then with water, and dried. It was found to boil at 205°, and analysis showed conclusively that it was nothing but *nitrobenzene*. It is difficult to explain this result, but it seems possible that nitroquinone is formed on treating the solid compound with water, but that it at once decomposes with regeneration of nitrobenzene. Various attempts were made to obtain the nitroquinone presumably formed, but without success.

The results of the experiments briefly described above lead us to doubt the existence of Étard's "nitroquinone," but part of our work affords a possible explanation of his statements. In one set of experiments we used a quantity of nitrobenzene, sold as pure, without taking the precaution of specially purifying it. When chromium oxychloride was added to an excess of this nitrobenzene heated to about 160°, the addition of each drop caused a violent reaction; quantities of hydrogen chloride were evolved, and finally an almost solid mass was formed in the flask. This was washed repeatedly with dry carbon bisulphide, which removed a considerable quantity of unaltered nitrobenzene, while a brown powder was left undissolved. When thrown into water, this compound was decomposed with evolution of heat, and a green solution was obtained. This was heated to boiling, and excess of sodium carbonate added to precipitate the chromium. The clear, yellow filtrate was evaporated to small bulk and acidified with hydrochloric acid. On cooling, a solid crystallised out in the form of pale-yellow leaves with a pearly lustre, which melt at 238°. When heated cautiously, the substance sublimes in brilliant, almost colourless needles. On analysis the following results were obtained:—

0·2546 gram substance gave 0·0726 gram H_2O (= 0·00806 gram H) and 0·4660 gram CO_2 (= 0·1276 gram C.).

0·44 gram substance gave 30·8 c.c. N at 14° and 750 mm.

	Calculated for $C_6H_4(NO_2)\cdot COOH$.	Found.
C.........	50·29 per cent.	50·11 per cent.
H	2·99 ,,	3·16 ,,
N.........	8·38 ,,	8·50 ,,
O.........	38·34 ,,	—

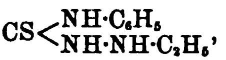
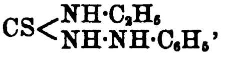
This result was confirmed by an analysis of the silver salt, which was found to contain 38·99 per cent. Ag, theory demanding 39·05 per cent. The substance was therefore *paranitrobenzoic acid.*

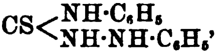
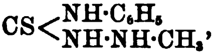
A brown chromium compound, similar to that just described, was obtained, but in much larger quantity, when a 50 per cent. solution of chromium oxychloride in chloroform or carbon bisulphide was heated with a similar solution of the impure nitrobenzene, hydrogen chloride being evolved. In this case, however, when the chromium compound was decomposed with water, nitrobenzene was obtained as well as paranitrobenzoic acid, and in proportionally large quantity. On examining the so-called pure nitrobenzene used in these experiments, we found it to contain a considerable amount of nitrotoluene, and it is evident that the paranitrobenzoic acid was produced by the action of chromium oxychloride upon this, and not from the nitrobenzene. Incidentally, therefore, we have confirmed von Richter's results, and perhaps we may venture to make the suggestion that Étard's "nitroquinone" was really paranitrobenzoic acid, produced by using nitrobenzene containing some nitrotoluene.

Chemical Laboratory,
University of Glasgow.

XVII.—*Semithiocarbazides.*

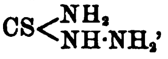
By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Galway.

In a previous communication which I had the honour to make to this Society (Trans., 1889, **55**, 303), I called attention to the remarkable difference which exists between two closely-related semithiocarbazides. The one, phenylethylsemithiocarbazide,  $\mathrm{CS}<\begin{matrix}\mathrm{NH\cdot C_6H_5}\\ \mathrm{NH\cdot NH\cdot C_2H_5}\end{matrix}$, described by Fischer (*Annalen*, **199**, 296) is stated as melting at 109—110°; whilst the other, ethylphenylsemithiocarbazide,  $\mathrm{CS}<\begin{matrix}\mathrm{NH\cdot C_2H_5}\\ \mathrm{NH\cdot NH\cdot C_6H_5}\end{matrix}$, described by myself in the communication already mentioned, melts between 121° and 122°.

On referring to the literature of the subject, with a view to ascertain whether a corresponding difference was observable between the properties of other isomeric forms of this class of compound, I found that, with the exception of those described by myself, only two disubstituted semithiocarbazides had hitherto been recorded. They are: (1) the above-mentioned phenylethylsemithiocarbazide, and (2) diphenylsemithiocarbazide,  $\mathrm{CS}<\begin{matrix}\mathrm{NH\cdot C_6H_5}\\ \mathrm{NH\cdot NH\cdot C_6H_5}\end{matrix}$, also obtained by Fischer (*Annalen*, **190**, 122). A third has since been added, namely, phenylmethylsemithiocarbazide,  $\mathrm{CS}<\begin{matrix}\mathrm{NH\cdot C_6H_5}\\ \mathrm{NH\cdot NH\cdot CH_3}\end{matrix}$, by G. v. Brüning (*Annalen*, **253**, 5—14).

The immediate object of the present investigation was to ascertain the reality, or otherwise, of the supposed isomerism in this series, by the preparation and examination of other compounds of this class; and, if established, to endeavour to trace some connection between their melting points.

The semithiocarbazides result from the action of the thiocarbimides on the substituted hydrazines; if the latter are monosubstituted, the product is a disubstitution-derivative, in which we may fairly assume that the position of the two substituting groups is fixed and determinate.

If we represent the type of a semithiocarbazide by the general formula  $\mathrm{CS}<\begin{matrix}\mathrm{NH_2}\\ \mathrm{NH\cdot NH_2}\end{matrix}$, we see that, whilst no less than *eight* different disubstitution-products are theoretically possible,* two, at most,

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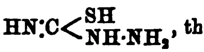
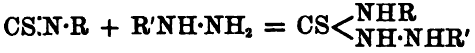
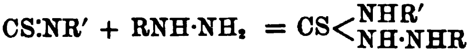
* If the type be  $\mathrm{HN{:}C}<\begin{matrix}\mathrm{SH}\\ \mathrm{NH\cdot NH_2}\end{matrix}$, the isomerides possible are *twelve* in number.

should result from the method of formation alluded to. Thus the combination may be represented as occurring either according to the equations—

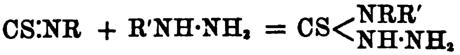


$$(a.)\ \mathrm{CS{:}N\cdot R + R'NH\cdot NH_2 = CS}<\begin{matrix}\mathrm{NHR}\\ \mathrm{NH\cdot NHR'}\end{matrix}$$

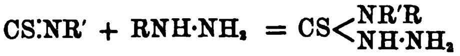


$$(a'.)\ \mathrm{CS{:}NR' + RNH\cdot NH_2 = CS}<\begin{matrix}\mathrm{NHR'}\\ \mathrm{NH\cdot NHR}\end{matrix}$$

or

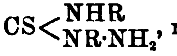


$$(b.)\ \mathrm{CS{:}NR + R'NH\cdot NH_2 = CS}<\begin{matrix}\mathrm{NRR'}\\ \mathrm{NH\cdot NH_2}\end{matrix}$$



$$(b'.)\ \mathrm{CS{:}NR' + RNH\cdot NH_2 = CS}<\begin{matrix}\mathrm{NR'R}\\ \mathrm{NH\cdot NH_2}\end{matrix}$$

The products of the second pair of reactions would be identical: that this is not the case, and therefore that these equations do not correctly represent the interaction, will be shown later on.

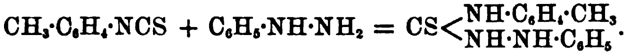


A similar type of compound, $\mathrm{CS}<\begin{matrix}\mathrm{NHR}\\ \mathrm{NR\cdot NH_2}\end{matrix}$, may also result, theoretically, from a different interaction; but in this case also, only *two* members of similar structure would be formed.

While dealing with the isomerism of the semithiocarbazides, I have also taken the opportunity of extending our general knowledge of this class of compounds, by filling in some of the vacant places in the series. The results are recorded below.

Orthotolylthiocarbimide and Phenylhydrazine.—Orthotolylphenylsemithiocarbazide.

Phenylhydrazine, dissolved in about its own volume of dry alcohol, was mixed with the quantity of orthotolylthiocarbimide demanded by the equation—



$$\mathrm{CH_3\cdot C_6H_4\cdot NCS + C_6H_5\cdot NH\cdot NH_2 = CS}<\begin{matrix}\mathrm{NH\cdot C_6H_4\cdot CH_3}\\ \mathrm{NH\cdot NH\cdot C_6H_5}\end{matrix}.$$

The substances combined energetically, so much heat being evolved that a portion of the alcohol was at once boiled off. On cooling, the mixture set to a brittle, pink, crystalline mass, which, on exposure to air, became first red and then deep green. After three recrystallisations from boiling concentrated alcohol, the substance was obtained in vitreous prismatic crystals, permanent in air, and which, when seen in mass, were of a very faint, delicate, pink tinge.

It was now analysed, with the following results:—

0·1868 gram, burnt with copper oxide, and copper gauze in front, afforded 25·8 c.c. nitrogen at 12° and 760 mm., or N = 16·39 per cent.

0·2146 gram, evaporated to dryness in a nickel crucible with sodium hydroxide, and fused with potassium nitrate* gave 0·1988 gram $BaSO_4$, or S = 12·73 per cent.

	Calculated for $C_{14}H_{15}N_3S$.	Experiment.
N	16·38	16·39
S	12·46	12·73

Orthotolylphenylsemithiocarbazide melts between 162° and 163°, with evolution of gas. It is nearly insoluble in water; moderately soluble in boiling alcohol, somewhat sparingly in cold; soluble also in ether and sparingly in chloroform. The alcoholic solution is not desulphurised by boiling with alkaline lead tartrate. Silver nitrate produces a white precipitate, which on the addition of ammonia, slowly darkens. On boiling with caustic soda, and adding solution of copper sulphate, a black precipitate forms, but no cuprous oxide is produced. The substance dissolves in concentrated sulphuric acid giving a pure azure-blue liquid resembling ammoniacal sulphate of copper in colour. The solid, treated with a drop of concentrated nitric acid, gives an intense orange-red colour, with evolution of gas. Ferric chloride, added to the alcoholic solution, produces a blood-red coloration, and copper sulphate, an intense, dirty green.

Phenylthiocarbimide and Orthotolylhydrazine.—Phenylorthotolylsemithiocarbazide.

Warm alcoholic solutions were mixed, containing molecular proportions of phenylthiocarbimide and orthotolylhydrazine. Almost immediately glittering prisms began to separate, and in a few moments the mixture solidified to a carrot-coloured mass, which on exposure to the air, slowly changed to greenish-blue. The colour-change is merely superficial, as, on washing with a little alcohol, the mass became white. The yield is quantitative.

On purification by repeated crystallisation from boiling alcohol, the substance was obtained in long, shining, white prisms, of a pearly lustre, melting at 145—146° with simultaneous copious evolution of gas.

The following results were obtained on analysis:—

0·1858 gram, burnt with CuO, and copper gauze in front, gave 25·7 c.c. nitrogen at 14·5° and 759·5 mm., or N = 16·22 per cent.

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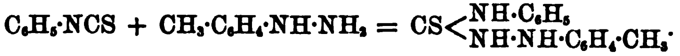
* In a previous communication (Trans., 1888, 53, 414), I mentioned this method as the one regularly employed by Professor Emerson Reynolds for the determination of sulphur (and halogens) in suitable compounds. The process is easily carried out, and affords excellent results in practice.

0·2252 gram, treated with NaOH and KNO_3, afforded 0·1989 gram $BaSO_4$, or S = 12·14 per cent.

	Calculated for $C_{14}H_{15}N_3S$.	Experiment.
N	16·38	16·22
S	12·46	12·14

The equation representing the reaction may be written thus:—



$$C_6H_5{\cdot}NCS + CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2 = CS{<}\begin{matrix}NH{\cdot}C_6H_5\\NH{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3\end{matrix}.$$

Phenylorthotolylsemithiocarbazide is almost insoluble in water, easily soluble in hot alcohol, moderately in cold; and freely in ether and chloroform.

The alcoholic solution gives, with silver nitrate, a white, curdy precipitate, which blackens slowly on standing, or immediately on addition of ammonia. It is also desulphurised, but very slowly, by boiling with alkaline solution of lead tartrate. With ferric chloride, a rich mahogany-red colour is produced. The substance dissolves readily in boiling caustic soda; on addition of copper sulphate to the hot solution, a black precipitate separates, but no cuprous oxide is formed. The solid, dissolved in cold concentrated sulphuric acid, yields a greenish-blue solution; with concentrated nitric acid an intense orange-red colour is produced, with evolution of gas. Copper sulphate gives a copious dark olive-green precipitate, which blackens on boiling.

On comparing the properties of the two compounds just described, it is evident that, although in the main—as might perhaps have been expected—they resemble one another somewhat closely, still the wide difference, 17°, between the melting points of the pure substances at once shows that they are not identical.

For convenience I here append a comparative table, showing some of their chief points of difference—

	$CS{<}\begin{matrix}NH{\cdot}C_7H_7\\NH{\cdot}NH{\cdot}C_6H_5\end{matrix}$.	$CS{<}\begin{matrix}NH{\cdot}C_6H_5\\NH{\cdot}NH{\cdot}C_7H_7\end{matrix}$.
Melting point.............	163°	146°
Solubility in hot alcohol....	Moderately soluble	Freely soluble.
Solubility in chloroform....	Moderately soluble	Freely soluble.
Colour with H_2SO_4........	Azure blue............	Greenish-blue.
Alkaline lead solution......	Not desulphurised	Very slowly desulphurised.

Methylthiocarbimide and Phenylhydrazine.—Methylphenylsemithiocarbazide.

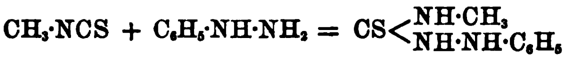
Methylthiocarbimide and phenylhydrazine, in molecular proportion, were mixed in hot alcoholic solution; the odour of the thiocarbimide at once vanished, and on concentration tufts of white needles separated, which were washed with alcohol and recrystallised twice from dilute spirit. Thus purified, the product forms delicate, silky needles, snow-white in colour, and melting between 88° and 89°. By slow crystallisation from dilute alcohol at the ordinary temperature, the substance can be obtained in very fine, large, trimetric prisms.

A sulphur determination was made, with the following result:—

0·3073 gram, treated with NaOH and KNO_3, afforded 0·2720 gram $BaSO_4$, or, S = 18·03 per cent.

Calculated for $C_8H_{11}N_3S$, S = 17·69 per cent.

The reaction is thus formulated:—



$$CH_3{\cdot}NCS + C_6H_5{\cdot}NH{\cdot}NH_2 = CS{<}\begin{matrix}NH{\cdot}CH_3\\ NH{\cdot}NH{\cdot}C_6H_5\end{matrix}$$

and the yield amounted to 68 per cent. of the theoretical.

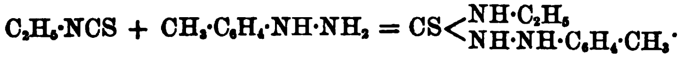
Methylphenylsemithiocarbazide is scarcely soluble in cold water, somewhat soluble in hot; very soluble in hot alcohol, moderately in cold; soluble in ether, and freely soluble in chloroform. The solution is not desulphurised even on prolonged boiling with alkaline lead tartrate. The solid dissolves in cold concentrated sulphuric acid, giving a rich azure-blue solution; another portion treated with a drop of strong nitric acid is vigorously decomposed with evolution of gas and production of a deep orange-red colour.

Ferric chloride, added to the solution, produces a deep greenish-blue colour, the mixture becoming after some time brown and turbid. Copper sulphate gives an intense deep-blue colour, not destroyed by boiling.

In a paper already referred to, G. v. Brüning records the preparation of a phenylmethylsemithiocarbazide, obtained from phenylthiocarbimide and methylhydrazine in aqueous solution: this substance is stated to melt at 143°; it is soluble in water and alcohol, and its aqueous solution is decomposed by mineral acids. It is accordingly isomeric with the methylphenylsemithiocarbazide described above. The difference, 54°, between the melting points is very remarkable.

Ethylthiocarbimide and Orthotolylhydrazine.—Ethylorthotolylsemithiocarbazide.

Warm alcoholic solutions of ethylthiocarbimide and orthotolylhydrazine were mixed in quantities required by the equation:—



$$C_2H_5{\cdot}NCS + CH_3{\cdot}C_6H_4{\cdot}NH{\cdot}NH_2 = CS<\begin{matrix}NH{\cdot}C_2H_5\\ NH{\cdot}NH{\cdot}C_6H_4{\cdot}CH_3\end{matrix}.$$

The mixture became deep-red, and, on concentration at the temperature of the air, crystals separated. The latter, when collected and pressed, formed a deep brownish-red cake, which, on washing with alcohol, became pink. When recrystallised twice from boiling alcohol, in which it is freely soluble, the substance was obtained in slender, white needles, having a very faint pink tinge and melting between 129° and 130°.

A sulphur estimation gave the following result:—

0·2551 gram, treated with NaOH and KNO_3, afforded 0·2904 gram $BaSO_4$, or S = 15·65 per cent.

Calculated for $C_{10}H_{15}N_3S$, S = 15·32 per cent.

Ethylorthotolylsemithiocarbazide is almost insoluble in cold water; very soluble in hot alcohol, rather soluble in cold; and freely soluble in ether and in chloroform.

With silver nitrate, the alcoholic solution gives a white precipitate which gradually darkens on standing. With ammoniacal silver nitrate, a yellow precipitate is produced which soon blackens; but the solution is not desulphurised by boiling with alkaline solution of lead. With ferric chloride, a clear, reddish-brown colour is produced, and with copper sulphate, an intense prussian-blue which darkens on boiling. The substance dissolves in sulphuric acid to form a rich azure-blue solution; and in concentrated nitric acid with effervescence, giving a dark brownish-red colour.

Allylthiocarbimide and Phenylhydrazine.—Allyphenylsemithiocarbaside.

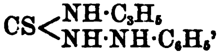
Allylthiocarbimide and phenylhydrazine, in molecular proportion, were mixed in somewhat dilute alcoholic solution. The mixture became warm, and the pungent odour of the oil of mustard almost disappeared: but the product was an oily liquid, which, even after several weeks, showed no tendency to solidify.

An attempt was next made to purify the product by suspending in water the mercurial derivative (obtained as a whitish, curdy precipitate by adding excess of mercuric chloride to the alcoholic solution) and treating with sulphuretted hydrogen. This process proved unsatisfactory, but the substance was eventually obtained in the solid condition by the following method.

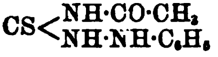
The base and thiocarbimide, in molecular proportions, were separately dissolved in benzene, and then carefully mixed, the containing vessel being well cooled by immersion in water. After allowing the whole to stand for some time, the reaction was completed by gently warming on the water-bath. At the end of a week the product had thickened to a tarry-looking, pulpy mass, which was washed slightly with cold benzene, and pressed between folds of bibulous paper. After recrystallising the residue twice from boiling benzene (in which it is very freely soluble), the substance was obtained in the form of a tangled mass of long, flexible, silvery-white needles, melting at 118—119° to a bluish-green liquid. The needles, on bruising, fall to a light, white, lustrous powder, which, on slight friction with a spatula, becomes very highly electrical, the particles scattering in all directions.

The formula was checked by a sulphur determination:—

0·2166 gram, treated with NaOH and KNO_3, afforded 0·2387 gram $BaSO_4$, or S = 15·15 per cent.

Calculated for  $CS<\begin{matrix}NH\cdot C_3H_5\\NH\cdot NH\cdot C_6H_5\end{matrix}$, S = 15·47 per cent.

Allylphenylsemithiocarbazide is soluble in water, and very freely in alcohol and ether. It dissolves freely in hot benzene, moderately in cold; the benzene solution is precipitated by light petroleum. The alcoholic or aqueous solution is blackened at once by ammoniacal silver nitrate; when heated with alkaline lead solution, the liquid assumes a yellowish-red colour, but is scarcely desulphurised even on prolonged boiling. The addition of copper sulphate produces an intense indigo-blue coloration; on heating, this is destroyed, with production of a black precipitate. Ferric chloride gives a clear, mahogany-brown colour. The solid acts like most of its congeners with sulphuric acid, the concentrated acid dissolving it readily with formation of a rich, deep azure-blue colour. Strong nitric acid, added to the solid, attacks it violently, the mixture becoming an intense orange-red.

It may be noted here, that ethylphenylsemithiocarbazide (Trans., 1889, **55**, 302), although it reacts like the preceding compounds with nitric acid, dissolves in concentrated sulphuric acid without producing any colour-change; whilst acetylphenylsemithiocarbazide,  $CS<\begin{matrix}NH\cdot CO\cdot CH_3\\NH\cdot NH\cdot C_6H_5\end{matrix}$ (*ibid.*, 303), and benzoylphenylsemithiocarbazide (*ibid.*, 304) give no colour reaction with either acid. The two latter compounds react with ferric chloride and copper sulphate, the acetyl-compound giving with ferric chloride a rich, blood-red colour, and with copper sulphate a dirty-greenish precipitate; whilst the benzoyl-derivative produces with ferric chloride a yellow, and with copper sulphate a dirty bottle-green colour.

In order to ascertain whether, in the case of these similarly-constituted compounds, Carnelley's rule—that, for isomeric compounds, the greater the solubility the lower the melting point—could be extended, I have directly determined the solubilities of a number of the semithiocarbazides described in this and the preceding communication, and where possible tabulate the results.

In column I (below) are the compounds, arranged in pairs for the purpose of comparison. Each semithiocarbazide, for shortness, is represented only by its substituting groups, the first of which indicates the thiocarbimide, and the second the hydrazine, with which the former is combined. Thus PhTo, for example, represents the compound $CS{<}\begin{matrix}NH\cdot C_6H_5\\ NH\cdot NH\cdot C_7H_7\end{matrix}$, obtained from phenylthiocarbimide and tolylhydrazine.

In column II, the melting point is given, corresponding to each substance; whilst the third column, III, records the order of solubility of each pair, the more soluble being marked 1, and the less soluble 2.

I.	II.	III.	I.	II.	III.
Compound.	M. p.	Order of solubility.	Compound.	M. p.	Order of solubility.
PhTo	146°	1	MePh........	89°	1
ToPh	163	2	EtPh	122	2
PhEt	110°	1	MePh........	89°	1
EtPh	122	2	PhTo........	146	2
EtTo.........	130°	1	MePh........	89°	1
PhTo	146	2	ToPh........	163	2
EtTo.........	130°	1	EtPh	122°	1
ToPh	163	2	PhTo........	146	2
EtPh	122°	2	EtPh	122°	1
EtTo.........	130	1	PhPh........	177	2
MePh	89°	1	AcPh........	179°	1
EtTo.........	130	2	BzPh........	over 220°	2

From this table, which includes all the compounds for which I have sufficient data for comparison, it is evident that the rule holds fairly;

the 12 cases presenting only a single exception, namely, the ethyl phenyl and ethyl tolyl pair.

A certain amount of connection is also observable between the various melting points and the corresponding molecular structure.

Carnelley has shown, in a large number of cases, that the melting points of similar compounds are connected with the symmetry or compactness with which the atoms are arranged in the molecule; the more symmetrical or compact molecules exhibiting higher resistance to fusion than those in which the atoms are less symmetrical or compact.

In attempting to apply this hypothesis to the semithiocarbazides, the thiocarbonyl-group, —CS—, may be regarded as a kind of nucleus or point about which the groups are balanced in the structure and loading of the molecule. The molecule in this case is symmetrical as regards two NH-groups; the first derived from the thiocarbimide, and the second from the hydrazine; whilst with respect to the third NH, that of the hydrazine, it is unsymmetrical.

This symmetry (or want of it) refers only to the *number* of groups existing between the simplest radicles at the extremities, and the thiocarbonyl nucleus. But the compounds may also be more or less symmetrical with respect to the *nature* of the terminal radicles. Thus, a disubstitution-derivative containing, for example, two aromatic or two fatty groups, would, *cæteris paribus*, be more symmetrical in this sense than another containing one fatty and one aromatic. The latter kind of symmetry may be referred to in this connection as *homogeneity;* it appears to influence the melting point considerably. Finally, the compounds may present more or less symmetry with respect to distribution of *weight* about the —CS— nucleus.

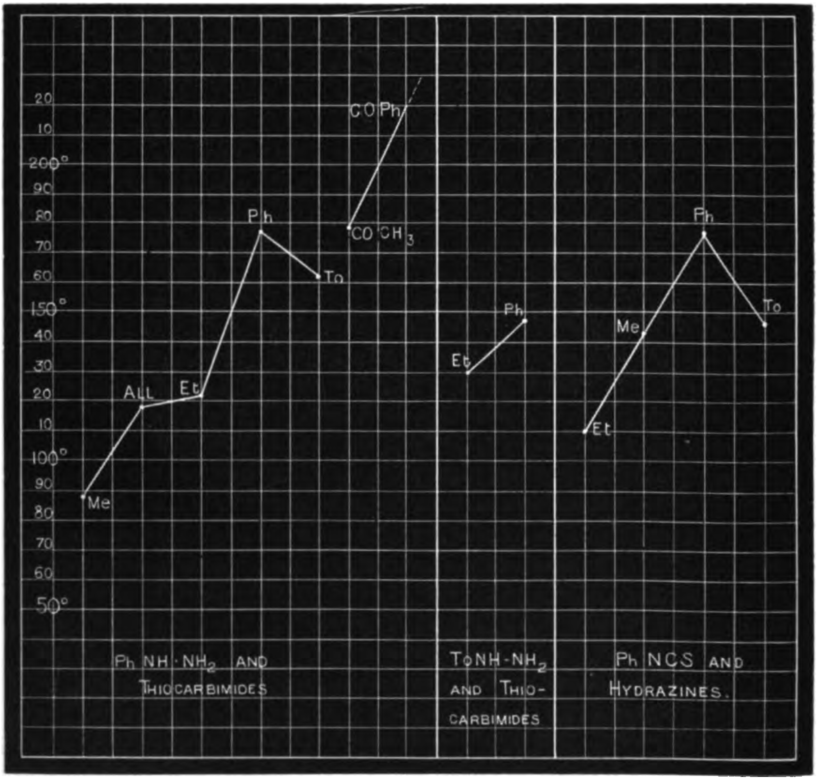
Thus, if the isomeric compounds (*a*) $CS{<}\begin{smallmatrix}NH\cdot CH_2\cdot CH_3\\ NH\cdot NH\cdot C_6H_5\end{smallmatrix}$ and (*b*) $CS{<}\begin{smallmatrix}NH\cdot C_6H_5\\ NH\cdot NH\cdot CH_2\cdot CH_3\end{smallmatrix}$ be considered it is evident that the group-symmetry of the former is superior to that of the latter. In *a* three groups balance one another about the nucleus; NH, CH_2, and CH_3, against NH, NH, and C_6H_5; while in *b* there are but two groups on one side—NH, C_6H_5—against four on the other—NH, NH, CH_2, and CH_3.

a Melts at 122°; *b* at 110°.

Similarly the molecule $CS{<}\begin{smallmatrix}NH\cdot C_6H_4\cdot CH_3\\ NH\cdot NH\cdot C_6H_5\end{smallmatrix}$ is more symmetrical than the isomeric $CS{<}\begin{smallmatrix}NH\cdot C_6H_5\\ NH\cdot NH\cdot C_6H_4\cdot CH_3\end{smallmatrix}$. The melting point of the former is 163°; that of the latter 146°.

It may happen that two molecules are equally symmetrical, as far as the atomic grouping is concerned, no matter how the terminal radicles are arranged. Here it would seem as though weight-symmetry was the factor determining the relative melting points. Thus, in the molecules (*c*) $CS<{NH\cdot C_6H_5 \atop NH\cdot NH\cdot CH_3}$ and (*d*) $CS<{NH\cdot CH_3 \atop NH\cdot NH\cdot C_6H_5}$ there are no open chains of atoms beyond those actually forming the semithiocarbazide skeleton; and if the C_6H_5 group be regarded as a unit playing a similar part to CH_3, they are equally symmetrical. But not so with respect to weighting; the load is more symmetrically distributed in *c*, where $NH\cdot C_6H_5$ balances $NH\cdot NH\cdot CH_3$, than in *d*, where $NH\cdot CH_3$ on one side is opposed to $NH\cdot NH\cdot C_6H_5$ on the other. The former melts at 144°, the latter at 89°.

A similar connection between fusibility and symmetry or homogeneity appears to hold also, in the main, in the case of *c* the combinations of a given hydrazine with various thiocarbimides, and *d* of a given thiocarbimide with various hydrazines.



Thus the compound of phenylhydrazine with *methyl*thiocarbimide melts at 89°; with *ethyl*thiocarbimide, at 122°; with *phenyl*thiocarbimide, at 177°. The latter compound is the most homogeneous possible for phenylhydrazine, and accordingly, in the next compound —with *tolyl*—even the similarity of the groups and the increased molecular weight fail to raise the melting point, which falls to 163°. The latter compound, while equally symmetrical with the *ethyl*-derivative, is more homogeneous; it melts 41° higher. In the case of *acetyl*- and *benzoyl*-phenylsemithiocarbazides a similar behaviour is shown. The former, $CS<{NH\cdot CO\cdot CH_3 \atop NH\cdot NH\cdot C_6H_5}$, melts at 179°; in the latter the increased homogeneity (as well as molecular weight) makes its influence strongly felt: this compound does not melt at 220°. Tolylhydrazine gives, with *ethyl*-thiocarbimide, a product melting at 130°; on exchanging the ethyl-group for *phenyl*, the melting point rises to 146°. Want of time and material have hitherto prevented my preparing the homogeneous and symmetrical ditolyl-compound; but it will probably be found, when obtained, to melt at a still higher temperature.

The semithiocarbazides derived from phenylthiocarbimide and various hydrazines show a like connection. The *methyl*-derivative melts at 143°; the loss of group symmetry, without any counterbalancing gain in homogeneity, tells in the *ethyl* compound, which melts at 110°. The homogeneous diphenyl reaches 177°; whilst, just as in the case of the isomeric compound (*ante*), the *tolyl*-derivative, notwithstanding the increased molecular weight, fails to reach the point of the more symmetrical and more homogeneous compound, and the melting point sinks to 146°—a fall of over 30°.

The compounds of ethylthiocarbimide with phenyl- and tolylhydrazines respectively, present some difficulty. The former, $CS<{NH\cdot CH_2\cdot CH_3 \atop NH\cdot NH\cdot C_6H_5}$, melts at 122°; the latter, $CS<{NH\cdot CH_2\cdot CH_3 \atop NH\cdot NH\cdot C_6H_4\cdot CH_3}$, at 130°. As the phenyl-derivative is more symmetrical than the tolyl-, it might have been expected that the latter would have been the more fusible. I am unable at present to offer any satisfactory explanation of this anomaly; it is worthy of note that this pair of compounds also exhibits irregularity as regards connection of solubility with fusibility.

XVIII.—*Note on a Phenylic Salt of Phenylthiocarbamic Acid.*

By Augustus E. Dixon, M.D., Professor of Chemistry, Queen's College, Galway.

PHENYLTHIOCARBIMIDE and pure phenol, in molecular proportion, were heated in a sealed tube for two hours, at 140—150°. The product, a mobile, brown liquid, smelling of both constituents, gradually deposited small, hard crystals; these, after being well washed with alcohol, pressed, and dried, melted between 149° and 151°.

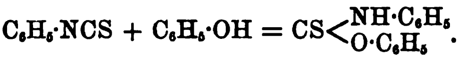
A determination of sulphur was made with the following result:—

0·2145 gram, treated with NaOH and KNO_3, afforded 0·2103 gram $BaSO_4$,

or, S = 13·48 per cent.

Calculated for $C_{13}H_{11}NSO$, S = 13·99 per cent.

The interaction is thus formulated:—



$$C_6H_5{\cdot}NCS + C_6H_5{\cdot}OH = CS{<}\begin{matrix}NH{\cdot}C_6H_5\\O{\cdot}C_6H_5\end{matrix}.$$

The yield is very small, not more than 7 per cent. of the theoretical; heating for four hours at 150°, or for two hours at 200°, reduced it still further.

Phenylic phenylthiocarbamate, obtained as above, occurs in small, well-formed, octohedral crystals resembling sulphur in appearance and colour.

It is almost insoluble in water, but dissolves in alcohol; the alcoholic solution gives a black precipitate with ammoniacal nitrate of silver, and is also freely desulphurised by warming with alkaline lead tartrate. On heating, either alone, or with caustic soda, it is readily decomposed with evolution of phenylthiocarbimide.

It is right to add that all the experimental work in connection with the present communication was carried out in the Chemical Laboratory of Trinity College, University of Dublin.

Chemical Laboratory, Queen's College,
Galway.

XIX.—*Behaviour of the more Stable Oxides at High Temperatures.* (Part I.) *Cupric Oxide.*

By G. H. **Bailey**, D.Sc., Ph.D., and W. B. **Hopkins**, the Owens College.

From a number of statements which occur in works on metallurgy, and observations made on changes which take place when cupric oxide is exposed to high temperatures, it is quite evident that under such circumstances there is a loss of oxygen. In most cases the observer has contented himself with stating that the product obtained is cuprous oxide, without giving the grounds on which this conclusion is based. On the other hand, however, there exist records of experiments in which the conditions of working and the products obtained are carefully described, and it will be of interest in regard to the results arrived at by us to give a brief *résumé* of the investigations which have been made on the lower oxides of copper. The earliest of these appeared in 1845 (*Compt. rend.*, **18**, 658), when Favre and Maumené, by heating cupric oxide at the temperature of melting copper, obtained a dark-coloured substance having the composition Cu_5O_3. Although oxygen was given off freely at this temperature, it was taken up again at a cherry-red heat.

Vogel and Reischauer (*Jahresb. Chem.*, 1859, 216) obtained cuprous oxide by heating cupric oxide, and Marchand (*J. pr. Chem.*, **20**, 505) found that on exposing cupric oxide in a muffle for half an hour at a white heat, and then for eight hours at a dull-red heat, the product remaining had the composition Cu_2O.

Without mentioning the many well-known reactions in which cuprous oxide is formed, it may be remarked that Gladstone and Tribe (*Chem. News*, **25**, 193) observed it as a yellow coating when a copper-silver couple was placed in a solution of nitrate of copper. The hydrated oxides prepared by Siewert (*Zeitschrift für Chemie*, 1866, 363), $Cu_3O_2,2H_2O$ and $Cu_4O_3,5H_2O$, and the tetrantoxide, Cu_4O (hydrated), of Rose (*Ann. Chem. Phys.*, **120**, 1) must also be mentioned.

With the exception of Rose's oxide, all these may be classified on the assumption that they are derivatives of cuprous and cupric oxides:—

Rose's oxide	Cu_4O
Cuprous oxide	Cu_2O (and cuprite).
Favre and Maumné's oxide	$2Cu_2O,CuO$.
Siewert's oxide (a)	$Cu_2O,CuO,2H_2O$.
„ „ (b)	$Cu_2O,2CuO,5H_2O$.

That cuprous oxide is obtained when cupric oxide is exposed in an oxidising atmosphere at a moderate temperature seems pretty conclusively shown.

Our object at the outset of this investigation was to examine whether cuprous oxide is the ultimate product when cupric oxide is exposed to high temperatures, or whether by using higher temperatures a further loss of oxygen took place.

Method of Experiment.

Finely-powdered cupric oxide was exposed to a white heat in a Fletcher injector-furnace, care being taken to preserve an oxidising atmosphere during the course of the experiment. At the temperature used, fire-clay crucibles were attacked by the copper oxide with the formation of a fusible slag, so that in most of the experiments recorded in this paper recourse was had to lime crucibles. As the temperature rose the oxide fused, and then bubbles of gas were seen to come off freely, the heating being continued—at least so long as there appeared to be any gas given off.

On cooling, a yellowish-red mass was obtained hard enough to scratch glass quite easily, and having the sp. gr. 3·81. A thin film of black oxide with which it was coated (and which evidently formed during the process of cooling down) was removed, though, indeed, it was so thin that it could hardly have affected the analytical determinations.

Analysis of Product.

The finely-powdered oxide was analysed by reduction in a stream of dry hydrogen, the water which was formed being absorbed in a calcium chloride tube in the usual manner, whilst the weight of copper remaining in the boat afforded a check on the results.

Several experiments were made, the time during which the oxide was exposed varying from one to three hours. In all cases the product obtained had the same properties and composition, the percentage of oxygen being always found to fall between 7 and 8 per cent.

A larger quantity was now prepared, the central portion of which was taken for analysis so as to be sure that no particles of lime had found their way into it. The results of the analysis were as follow :—

Substance taken..............	0·615	gram.
Water obtained	0·0535	„
Copper „	0·568	„
Copper (by difference)	0·5655	„

The percentage composition calculated from these numbers agrees well with that required for Cu_3O:—

	Found.	Calculated.
Copper............	92·36	92·23
Oxygen	7·73	7·77

For the sake of comparison, it may be stated that the oxides Cu_2O and Cu_4O contain 11·22 and 5·94 per cent. of oxygen respectively.

Although every care was taken to preserve an oxidising atmosphere in the furnace, further proof was deemed desirable that the loss of oxygen was not due to reducing action of the flame. A piece of hard lime was therefore hollowed out, and in this the oxide was exposed to the oxy-hydrogen or rather oxy-coal gas flame, in such a way that only the extreme point of the oxidising flame was allowed to play upon it. Fusion took place as before, and gas was observed to be given off; when the evolution of gas had ceased the mass was allowed to cool. The product in all respects resembled that obtained in the Fletcher furnace, and where it came in contact with the lime there was formed a bright vermilion coating which consisted of lime and a lower oxide of copper, but which was not further examined. The results of two determinations were:—

	I.	II.
Substance taken	0·564	0·494
Water obtained	0·045	0·042
Copper „	0·524	0·457
Copper (by difference) ...	0·524	0·456

We have thus:—

	I.	II.	Calculated.
Copper..........	92·90	92·51	92·23
Oxygen	7·09	7·55	7·77

The results of the analysis show that the product obtained at the higher temperature is substantially the same as that obtained at the lower, and that it therefore maintains a constant composition within a fairly wide range of temperature, the limits of which we consider are approximately 1500° and 2000° C.; at any rate platinum readily fuses at the higher temperature used. From this it appears that as the oxides of smaller stability give up oxygen at moderate temperatures, so the more stable oxides, such as oxide of copper, are transformed into lower oxides at higher temperatures without the intervention of any reducing agent. Furthermore, as the evidence of several experimenters seems conclusive that cuprous oxide is obtained when a dull-red heat is used, there is—especially if we include Rose's oxide—an indication that the points of stability occur at definite stages in the process of transformation into the lower oxide, since we have the series Cu_4O, Cu_3O, Cu_2O, CuO. And although our object in this research is rather to accentuate the behaviour of oxides when exposed to high temperatures, it does seem as though sufficient evidence existed for the assumption that Cu_3O may be regarded as a definite oxide of copper, especially when its properties as given below are taken into consideration.

Action of Reagents on Cu_3O.

Even when reduced to the finest state of division in an agate mortar, the oxide is entirely unacted on by concentrated (or dilute) mineral acids; even aqua regia and boiling concentrated sulphuric acid are without action. Hydrofluoric acid, however, slowly attacks it with the formation of a blue, crystalline fluoride of copper which has not been further examined. The only method by which we were able to bring the oxide into solution for the purpose of confirming the analysis by an entirely different process was to fuse it with caustic potash, in which it dissolved with a blue colour, and from which it separated again on the addition of water in flocculent, brown particles. This, dissolved in sulphuric acid and titrated with potassium permanganate, was found to contain 9·8 per cent. of oxygen, a result falling about midway between Cu_3O and Cu_2O; it was, however, to be expected that some oxidation would take place in the process of fusion and extraction with water; in spite of this, however, the product contained less oxygen than Cu_2O.

It would be interesting to analyse a number of samples of native cuprite in order to see if they yielded any indication of exposure to temperatures such as were used in these experiments. We are continuing the work and proceeding with the examination of other oxides, and have indeed already obtained evidence that litharge, sesquioxide of bismuth, and vanadic acid lose oxygen in the same way as cupric oxide.

XX.—*The Influence of different Oxides on the Decomposition of Potassium Chlorate.*

By G. J. Fowler, M.Sc., and J. Grant, the Owens College.

As several papers have recently appeared on this subject, it will be well to give some account of the origin and scope of the present work.

More than a year ago some experiments were made in this laboratory by J. Paul with a view to prepare pure oxygen from potassium chlorate. It was found that if the oxygen evolved was filtered through glass wool, before being collected over mercury, the latter remained quite clean on the surface when the gas was bubbled through it. Potassium chloride in considerable quantity was found in the glass wool, and no chlorine, or the merest trace, was evolved. It was found, however, that when silica or powdered glass was mixed with the chlorate, chlorine was given off in appreciable quantity. If, therefore, chlorine was given off at all on heating pure potassium chlorate, as some observers believed, its evolution appeared to be due to the action of a large surface of glass on the fused salt.

A few preliminary observations were then made on the effect of other substances, chiefly oxides, on the decomposition of potassium chlorate. The results obtained at that time seemed to be of sufficient interest to warrant a fuller inquiry. The work was therefore resumed later on, and a large number of experiments were made.

Since the beginning of the work, papers have been published by Hodgkinson and Lowndes, McLeod, and others which have added considerable interest to the question. These experimenters have confined themselves chiefly to the action of manganese dioxide on potassium chlorate under different conditions. Hodgkinson and Lowndes have examined the effects of other oxides to some extent, and have anticipated some of the results recorded in this paper. Their conclusion with regard to the action of manganese dioxide on potassium chlorate is as follows (*Chem. News*, **59**, 63): "The manganese dioxide is alternately reduced and reoxidised by the potassium chlorate, but only in exceptional instances is the reoxidation complete. This reduction in a strongly oxidising atmosphere is probably due to the atomic attraction of the oxygen; the oxygen-atoms in the chlorate and the dioxide pull at each other, and the force of attraction, combined with the decomposing effect of the temperature, is sufficient to break up both compounds." This theory, however, scarcely accounts for the evolution of chlorine which inevitably accompanies the oxygen.

McLeod (Trans., 1889, **55**, 184) comes to the conclusion that the manganese dioxide attacks the chlorate, forming potassium permanganate and liberating chlorine. The $KMnO_4$ decomposes by heat into K_2MnO_4, MnO_2, and O_2. The K_2MnO_4 is decomposed by fresh chlorine into KCl, MnO_2, and O_2, so that only a little chlorine is evolved and the manganese dioxide is constantly regenerated. If the evolution of chlorine is prevented by the addition of sodium carbonate, the oxygen is evolved at a much higher temperature. McLeod's theory of the action then is purely chemical.

Reference is made in McLeod's paper to work done by Baudrimont (*Journ. Pharm.* [4], **14**, 1871, 81, 161). This chemist has investigated the action of a number of oxides on potassium chlorate, notably manganese dioxide in various conditions, ferric oxide, and copper oxide, the temperature of evolution and the amount of chlorine evolved being noticed in each case. Baudrimont looks upon the action of manganese dioxide as being different from an ordinary chemical reaction, and speaks of it as an action by contact or presence, or as a catalytic action similar to the action of silver or platinum, silver oxide, or manganese dioxide on hydrogen peroxide. It should be mentioned that in a discussion on Baudrimont's paper (*loc. cit.*, 130), Jungfleisch puts forward much the same view of the action as McLeod, and draws attention to the formation of potassium permanganate by projection of manganese dioxide into fused chlorate.

Warren (*Chem. News*, **58**, 247) comes to the conclusion that only those oxides are active which are capable of forming higher oxides. He also believes that the evolution of chlorine may be due to the formation of a manganate in the case of manganese dioxide.

Veley (*Phil. Trans.*, 1888 [1], 271) draws attention to the action of finely-divided particles in promoting the evolution of gases from liquids, and considers the action of manganese dioxide upon potassium chlorate to be due—(i) to the finely-divided state of the manganese dioxide; (ii) to the chemical interaction between it and the chlorate.

Finally, Spring and Prost (*Bull. Soc. Chim.*, 1889, 340—342) have heated the chlorates of several metals in porcelain and platinum vessels in presence of carbon dioxide, silica, and phosphorus pentoxide.

They consider that the evolution of oxygen is an indirect phenomenon, the chlorate first splitting up into $M_2O + Cl_2O_5$. The Cl_2O_5 yields $Cl_2 + O_5$ when we have $M_2O + Cl_2 = 2MCl + O$. The reaction is incomplete if the chlorine is carried away by the violence of the reaction, or if the base forms a salt on which the chlorine has no action. A strong base (K_2O for example) may oxidise the Cl_2O_5, a perchlorate being formed.

From the foregoing summary of the work which has been done in this direction, it is sufficiently evident that no simple interpretation is to be expected of the reaction which takes place during the decomposition of potassium chlorate, and its character is manifestly largely influenced by the presence of other bodies.

Our object in this work has been to examine systematically the influence of the chief metallic oxides and certain unstable salts on the decomposition of potassium chlorate. We have determined in each case the temperature at which oxygen is evolved, the amount of chlorine given off, and the composition of the residue after heating. These results varied with the acid or basic character of the oxide, with its physical condition, and with the relative masses of oxide and chlorate, and by comparison of the data thus obtained, we have sought to arrive at a general explanation of the action, not only of manganese dioxide, but of other oxides which are effective in promoting the decomposition of potassium chlorate (either with or without evolution of oxygen).

Description of Apparatus.

The apparatus employed consisted of a sheet-iron cylinder, acting as an air-bath, 9 inches in height and 7½ in diameter. The lid was loose, and the bottom riveted on; in the movable lid were two circular holes at equal distances from the sides and centre. One of these was for the air-thermometer, a small glass bulb and tube of 30 c.c. capacity attached to a glass tube bent twice at right angles, and terminating in a manometer tube containing mercury. This was graduated by a mercurial thermometer up to 280°; the higher temperatures being calculated afterwards. It is probable that these values are somewhat too high; the numbers, however, are comparable among themselves, which is sufficient for the object we had in view. The other aperture in the lid admitted the chlorate bulb, to which was attached, by thick indiarubber, a long glass delivery tube, the gases being passed before collection through a solution of potassium iodide. Both bulbs reached to the centre of the cylinder. Two large Bunsen lamps were used, the flames of which surrounded the whole apparatus. Of course all care was taken to ensure that the same conditions, as nearly as possible, obtained throughout the series of experiments, as to heating arrangements, strength of potassium iodide solution, character of potassium chlorate used, &c. Indeed, with regard to the latter point, more than a pound of potassium chlorate was freed from chloride and other impurities, and finally recrystallised; this served for the whole of the series of experiments.

In the following experiments, statements regarding the amount of chlorine given off are expressed approximately in terms of the quantity evolved when one part of manganese dioxide is mixed with three parts of potassium chlorate. Exact quantitative measurements were not made, a rough comparison appearing sufficient for our purpose.

Oxides of Antimony, Tungsten, Uranium, and Vanadium.

The results of experiments with these oxides are summarised in the following table. The temperatures given in these and other experiments are those at which a moderately brisk evolution of oxygen began to take place.

I. No. of expt.	II. Formula of oxide.	III. Relative masses of oxide and chlorate.	IV. Temperature.	V. Remarks.
63 64 65	Sb_2O_5 " "	1 : 2 2 : 1 3 : 1	340° 430 440	Large quantity of chlorine in each case. On treating residue with hot water and filtering, potassium antimonate found in filtrate.
92 93	U_3O_8 "	1 : 2 2 : 1	390 390	Large quantity of chlorine evolved. Reddish-yellow residue dissolving to yellow solution of potassium uranate.
110	WO_3	1 : 2	250	Not so much chlorine as with V_2O_5. Potassium tungstate found in residue.
109	V_2O_5	1 : 2	150—170	Large quantity of chlorine. Red coloured residue soluble in water to golden-coloured solution of potassium metavanadate.

It will be noticed that the temperature of evolution is lower, the more acid the oxide.

It may be mentioned here that the slightest trace of an acid (such as nitric) is sufficient to break up the chlorate at a low temperature; for instance, bismuth sesquioxide has little action on potassium chlorate. From a mixture of 2 grams chlorate with 0·75 Bi_2O_3 and 0·25 $Bi(NO_3)_3$, oxygen is evolved quickly at 300°, together with chlorine. The action of nitric acid on the chlorate will of course be complicated.

Again, titanium dioxide containing a slight trace of sulphuric acid brings off the oxygen at a low temperature, whilst the pure oxide has but little action.

Oxides of Aluminium, Silicon, and Tin.

I.	II.	III.	IV.	V.
20	Al_2O_3	1 : 2	400°	4 units chlorine evolved.
42	SiO_2	1 : 2	400	4 units chlorine.
95	SnO_2	1 : 2	470	1 unit chlorine.

It will be seen that alumina and silica agree very closely in their properties (compare Mills, "On the Action of Oxides on Salts," *Journ. Chem. Soc.*, 1879, ii, 336). On extracting the residue, after heating, with water, an alkaline solution was obtained in both cases.

In the case of tin oxide, only a very small trace of tin could be dissolved out on treating the bulb contents with water, and the solution was not alkaline. Tin oxide, however, as is seen from the table, is not specially active. In this case the tin oxide used was prepared in the dry way, as it was found difficult to free the precipitated oxide from nitric acid. The greater activity of the precipitated oxide appeared to be partly due to this cause; after ignition it is not so active.

We may conclude that these oxides act upon the chlorate in the same manner as those of the last class. They are less active, however, according as the attraction between the oxide and K_2O is weaker.

Sesquioxides of Chromium, Antimony, and Arsenic.

With regard to these oxides there is not much further to be said. With all of them oxidation takes place, accompanied in the case of antimony and arsenic oxides by incandescence. Chromate, antimonate, and arsenate of potassium are formed. Chlorine is evolved in each reaction, most copiously in that produced by chromium sesquioxide.

Oxides of Manganese, Iron, Nickel, Cobalt, and Copper.

The monoxides of iron, nickel, cobalt, and manganese, and the suboxides of copper, are oxidised by the chlorate with explosive rapidity, a great rise of temperature taking place.

The reaction which is brought about by manganese dioxide has already been discussed. We may mention that at the outset of our experiments we noticed the pink colour of the permangate produced when a trace of manganese dioxide is fused with the chlorate.

What takes place in the case of the higher oxides of iron, cobalt, nickel, and copper, it is difficult directly to determine. The close agreement of their mode of action with that of manganese dioxide seems to point to an analogous reaction taking place. Higher oxides would seem to be formed in all cases; these combine with the K_2O to form unstable compounds which are broken up like the permanganate in the case of manganese dioxide.

The following table gives the results of some of the experiments made with *manganese dioxide*:—

I.	II.	III.	IV.	Cl evolved.	Remarks.
2	MnO_2.	1 : 3	370°	unit	With 2 and 3 there was a rush of gas.
3	”	1 : 4	330	less	
6	”	1 : 6	340	(same as 3)	In 6, 7, and 8 the same oxide was used. Powdered pyrolusite was made use of.
7	”	1 : 6	340	”	
8	”	1 : 6	340	”	
4	”	1 : 8	360	(less than above)	

The results show that the temperature of initial action is altered to some extent by variations in the ratio of oxide to chlorate. There is a certain ratio, however, which produces the most regular evolution of oxygen, this being one part manganese dioxide to six parts chlorate, with which there is a rapid and regular evolution at 340° to 360°. With smaller quantities of chlorate in proportion to the manganese, there is apt to be a rush of gas.

If the temperature be quickly raised, chlorine comes off more abundantly (see Warren, *Chem. News*, Nov., 1888, **58**, p. 247), apparently because the equilibrium is disturbed, there not being sufficient time for the chlorine to decompose the manganate.

The following are the results of some of the experiments made with *ferric oxide*:—

I.	II.	III.	IV.	Units of Cl evolved.	Remarks.
79	Fe_2O_3	1 : 6	380°	3½	Very rapid evolution.
10	$Fe_2(OH)_6$	1 : 2	440	2	Rapid evolution.
12	Fe_2O_3	2 : 1	280	less	” ”
13	$Fe_2(OH)_6$	4 : 1	380	much less	Steady evolution, less rapid.

With ferric oxide, more chlorine is evolved, and under certain conditions the oxygen comes off at a lower temperature than with manganese dioxide. In experiment 12, where this is the case, the oxide had been previously used; this seems to improve, rather than diminish its activity.

The relative masses of oxide and chlorate and the presence of water of hydration both have considerable influence on the temperature of evolution and on the quantity of chlorine given off. If sodium carbonate is added to the mixture of ferric oxide and chlorate, the temperature at which the oxygen is evolved is greatly increased as in the case of manganese dioxide.

The *sesquioxides of cobalt and nickel* resemble each other in their action very closely. The temperature of evolution is lower than with manganese dioxide and ferric oxide. With one part of Co_2O_3 to two parts of chlorate, a rush of gas took place at 250°. Less chlorine is given off than is the case with ferric oxide.

With *cupric oxide*, all the gas appears to come off with a rush at one particular temperature. Very little chlorine is evolved. In experiment 32, for example, one part of cupric oxide, previously used, was mixed with two of chlorate. At 350° no gas was coming over; at 360° it all came over with a rush, very little chlorine being evolved.

Baudrimont (*loc. cit.*) noticed that with cupric oxide the evolution of oxygen is accompanied by a rise of temperature, which seems to point to the breaking up of some compound formed with absorption of heat. Sodium carbonate in this case also checks the evolution of oxygen.

Oxides of Mercury, Silver, Lead, Barium, and Calcium.

Some interesting results were obtained with the above oxides. After heating each of them with potassium chlorate for a considerable time at a high temperature (about 500°), no gas (or only a mere trace) was evolved. The contents of the heating bulb were treated with boiling water, filtered, and both residue and filtrate examined. The filtrate in all cases contained potassium perchlorate.

Mercuric Oxide.—On heating mercuric oxide alone at 360° (in mercury vapour), it underwent no change. On mixing it with chlorate, however, and heating at the same temperature, a sublimate of metallic mercury was formed on the sides of the heating tube, and there was a slight loss of oxygen from the mixture. On dissolving the residue in water and filtering, potassium perchlorate was found in solution, and on passing sulphuretted hydrogen, sulphide of mercury was precipitated, showing that some mercuric chloride had been formed in the reaction.

Oxide of Silver.—Although the mixture of silver oxide and chlorate was heated for considerably over an hour at a temperature far above that at which silver oxide decomposes (270—280°), no evolution of gas took place. On treating the contents of the bulb with hot water and filtering, pure silver was left behind, and the filtrate contained large quantities of potassium perchlorate.

Peroxide of Lead.—After the first heating with chlorate, the washed residue is composed partly of the dioxide and partly of red lead. The second heating with fresh chlorate did not complete the conversion, but on a third trial the whole of the dioxide was transformed into red lead. Potassium perchlorate was formed in each case. At a very much higher temperature the Pb_3O_4 became reduced to PbO. A trace of chlorine was evolved in the above cases. If lead oxide is heated with excess of chlorate to a moderate temperature, the peroxide is formed, also potassium perchlorate, by a back reaction.

Oxides of Barium and Calcium.—When barium dioxide is heated with chlorate, a considerable quantity of potassium perchlorate is obtained; the barium dioxide is reduced. The monoxides of barium and calcium are oxidised to the peroxides, potassium perchlorate being still formed by a back reaction, but in smaller quantity than when the dioxide is used to begin with. In the case of barium dioxide, the temperature employed influences the quantity of perchlorate formed. Thus at 360° (mercury vapour) more perchlorate is formed than at 448° (sulphur vapour).

The influence of certain salts on the decomposition of the chlorate may be mentioned here as being of interest in connection with the foregoing experiments.

Permanganates of Potassium and Silver.

I.	II.	III.	IV.	V.	Remarks.
66	$KMnO_4$	1 : 2	370°	nil	Very rapid evolution.
67	"	2 : 1	360	unit	Rapid evolution.
69	$AgMnO_4$.	1 : 2	500	trace	Very rapid evolution.
70	"	2 : 1	490	trace	Rapid evolution.

The explanation of the action of the permanganates of potassium and silver is, no doubt, that at the high temperature the permanganates decompose, according to the following equations:—

$$2KMnO_4 = K_2MnO_4 + MnO_2 + O_2,$$
$$AgMnO_4 = Ag + MnO_2 + O_2.$$

The manganese dioxide then acts in the manner already described, but no chlorine is evolved, owing to its combination with potassium and silver.

Potassium Dichromate.

When potassium dichromate and potassium chlorate are heated together, the mixture first fuses, then gives off oxygen, without chlorine, accompanied by a great deal of frothing. The dichromate appears to suffer no change, except at a very high temperature, when a certain amount of chromate and perchlorate of potassium is obtained.

Potassium Nitrate.

On heating a mixture of potassium nitrate and chlorate, both oxygen and chlorine came over slowly. When the temperature is raised to dull redness, gas was evolved rapidly with much frothing. The residue left, after heating at this temperature for some time, contained a considerable amount of potassium nitrite.

From the foregoing experiments, it seems probable that, in all the cases considered, the influence of the oxide upon the decomposition of the chlorate is largely chemical, although, in some cases, physical causes help to bring about the result (Veley, *loc. cit.*).

The mode in which the chemical action proceeds depends upon several factors:

The affinity of the oxide for K_2O
" " " O
" " " $O + K_2O$
The affinity of the chlorate for O.

It will be readily seen that the problem is a complicated one. It is very difficult, in many cases, to determine the exact course of the reaction, as more than one may take place at once.

The above generalisations are illustrated by the following summary of our results :—

1. Acid oxides, such as V_2O_5, U_3O_8, WO_3, evolve oxygen at a reduced temperature, a metavanadate, tungstate, or uranate being formed. Chlorine is evolved, in these cases, in *large* quantity. The whole of the oxygen of the chlorate is not evolved, the compound of K_2O, with the oxide, not being decomposed by heat or by chlorine. Here it is evident that a leading factor in bringing about the reaction is the affinity of the oxide for K_2O.

2. Alumina probably acts like the above oxides, but less energetically, the attraction between the K_2O and Al_2O_3 not being so great.

3. In the case of chromium sesquioxide the oxygen comes off at a reduced temperature, accompanied by chlorine. The reaction would seem to be brought about here by the affinity of the Cr_2O_3 for O and the affinity of the CrO_3 thus formed for K_2O.

4. In the case of the sesquioxides of iron, cobalt, and nickel, cupric oxide, and manganese dioxide, oxygen is evolved at a comparatively low temperature, accompanied by only a little chlorine; the oxide is left but little altered at the end of the experiment. Here it is probable that an unstable equilibrium is produced, resulting in the decomposition of the chlorate.

Accepting McLeod's theory of the action of manganese dioxide (which is fully in harmony with our own results), it would seem that manganese dioxide acts, to begin with, by reason of its affinity for oxygen and the affinity of the higher oxide thus formed for K_2O. The permanganate first formed, however, is unstable (here there is a difference between the oxides of this class and those of the preceding); it splits up on heating into $K_2MnO_4 + MnO_2 + O_2$. *The* K_2MnO_4 *is decomposed by the fresh chlorine which is liberated* (Spring and Prost, *loc. cit.*) into KCl and MnO_2, which is thus regenerated. The addition of sodium carbonate retards the evolution of oxygen, probably because the manganate is thereby rendered more stable.

The action of the other oxides of this class can, we believe, be explained in a manner similar to that of manganese dioxide.

5. The oxides of barium, calcium, and lead cause no evolution of oxygen when heated with chlorate, but the latter breaks up below its normal temperature of decomposition, potassium chloride and a peroxide being formed. Here the affinity of the oxide for oxygen brings about the change.

6. On the other hand, potassium chlorate may act as a reducing agent in the presence of such oxides as silver oxide and the peroxides of barium and lead, a perchlorate being formed. No oxygen is evolved. Here the reaction is brought about by the affinity of the chlorate for oxygen. In the case of the oxides of calcium, barium, and lead, the extent to which the chlorate is oxidised or reduced evidently depends on the masses of the reacting substances.

7. We have found that water of hydration diminishes the activity of an oxide.

8. The physical condition of the oxide is of influence (see Wright and Luff, *J. Chem. Soc.*, 1878, p. 1). Copper oxide, prepared in the dry way, is almost inactive.

9. Certain bodies, which apparently undergo no chemical change whatever, yet assist the reaction, as powdered glass, sand, kaolin.

In this case the action of fine particles (see Veley, *loc. cit.*) is of influence, as it was found that the above-mentioned bodies lost their activity to a large extent when the more finely-divided particles were washed out.

10. Certain oxides, such as those of zinc and magnesium, are completely inactive.

XXI.—CONTRIBUTIONS TO THE CHEMISTRY OF THIOCARBAMIDES.

Interaction of Benzyl Chloride and Allyl Bromide, respectively, with Thiocarbamide, Monophenylthiocarbamide, and Diphenylthiocarbamide.

By **Emil A. Werner**, Assistant Lecturer in Chemistry, Trinity College, University of Dublin.

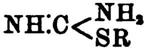
Introduction.

Soon after the discovery of thiocarbamide by Professor Emerson Reynolds, it was shown by Claus (*Ber.*, **7**, 236; *Ber.*, **8**, 41; *Annalen*, **179**, 145) that the amide can combine with iodide and bromide of ethyl to form compounds represented empirically by the formula $CSN_2H_4 \cdot C_2H_5X$;* since then, several compounds of the same class have been prepared and examined from time to time by different investigators.

Beyond showing that these compounds could yield basic substances on treatment with moist silver oxide, Claus never studied his products in any detail, the view that these are sulphine-compounds of similar constitution to the well known sulphine-derivatives of the thio-ethers being generally accepted as consistent with the symmetrical structure of thiocarbamide, viz., $NH_2 \cdot CS \cdot NH_2$.

Bernthsen and Klinger (*Ber.*, **11**, 492; **12**, 575), in their study of the compounds which thiocarbamide forms with methyl iodide, ethyl iodide, and benzyl chloride, showed that the bases resulting from the action of alkalis on these substances, are not hydroxyl-compounds, since they do not contain oxygen, water being eliminated in the interaction thus:—

$$CSN_2H_4 \cdot C_7H_7Cl + KOH = CSN_2H_3 \cdot C_7H_7 + KCl + H_2O,$$

and the bases are *isomeric* with the corresponding mon-alkyl substituted thiocarbamides. From certain reactions of these bases, and chiefly from their sharp decomposition into mercaptans and dicyandiamide when heated, these chemists proposed the formula  $NH{:}C{<}\genfrac{}{}{0pt}{}{NH_2}{SR}$ to represent their constitution, that is, alkyl salts of imidothiocarbamic acid, the original compounds being the haloïd salts.

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* Claus also obtained compounds of the composition $(CSN_2H_4)_2C_2H_5X$, but these do not enter into the present investigation.

Will, having first shown (*Ber.*, **14**, 1489) that symmetrical disubstituted thiocarbamides can also combine with alkylogens, the same chemist, in the following year (*Ber.*, **15**, 339), from the results of a detailed study of the compounds formed from thiocarbanilide and methyl and ethyl iodide, and from ethylene dibromide, corroborated the above constitutional formula of Bernthsen and Klinger.

Rathke, who had in the meantime (*Ber.*, **14**, 1776) re-examined Will's compound from thiocarbanilide and ethyl bromide, came also to the same conclusion respecting its constitution, and was the first to propose therefrom the unsymmetrical formula $NH{:}C{<}\genfrac{}{}{0pt}{}{NH_2}{SH}$ as probably representing the true structure of thiocarbamide itself. Will shortly afterwards (*Ber.*, **15**) proposed the same formula. It must be remembered, however, that the above is only an extension of the formula $NH{:}C{<}\genfrac{}{}{0pt}{}{NH_2}{OH}$, proposed, as far back as 1868, by Wanklyn and Gamgee (*J. Chem. Soc.*, **21**) to represent the structure of carbamide.

It is interesting to observe that no compound from a mono-substituted thiocarbamide had been prepared, and whilst Claus, Bernthsen, and Klinger were engaged solely with derivatives of the primary thiocarbamide, Will and Rathke, on the other hand, in more detailed investigations, confined themselves to compounds derived principally from diphenylthiocarbamide.

The incomplete and somewhat unsatisfactory information obtainable concerning the acting of the alkylogens on thiocarbamide and its different phenyl-derivatives led to the following detailed study of the subject, in order to accumulate further evidence bearing on the structure of thiocarbamide. The work described in the present paper has been carried out in Professor Reynolds' private laboratory in this University, where the same problem is being attacked from another side, with results which will shortly be published by Dr. Reynolds.

The phenylated thiocarbamides, besides being the easiest to obtain in a pure state, were chosen chiefly on account of their yielding products which in the majority of cases are easy to purify, this being of particular account where the products from decomposition reactions are to be studied; the same remarks apply to the choice of benzyl chloride as the alkylogen, whilst allyl bromide was used as the first instance of an unsaturated alkylogen being caused to interact with thiocarbamide.

I. *Interaction of Benzyl Chloride and Thiocarbamide.*

Before commencing a detailed study of the compound

$$CSN_2H_4{\cdot}C_7H_7Cl,$$

first described by Bernthsen and Klinger (*Ber.*, **12**, 575), it was necessary that I should repeat to a certain extent the work already carried out by these chemists; and particularly as their paper on this compound is remarkable for its brevity and entire absence of analytical data.

When equal molecular proportions of benzyl chloride and thiocarbamide are warmed on the water-bath in presence of a little alcohol, a reaction soon sets in which the heat evolved is sufficient to complete. On allowing the product to cool in an open vessel, preferably a flat-bottomed glass dish, the new substance separates, according to the degree of concentration, either in coherent, rosette-like aggregates, or in thin superposed plates; it is conveniently purified by recrystallisation from water or by gradual precipitation of its alcoholic solution with ether: in both cases it separates in small, well-defined, glistening prisms. The melting point, 166—168°, given by Bernthsen and Klinger, in itself indicates an impure compound. I find the substance, purified as above, to melt at 174° (uncorr.), from numerous determinations; at the same time, I have noticed specimens, on three occasions, to melt at 142—143°, a temperature which was independent of the rate of heating, and was never exhibited a second time, the resolidified product melting afterwards at 174°. The observation suggests the existence of polymeric modifications. Two chlorine estimations gave the following results:—

I. 0·282 gram gave 0·2009 gram AgCl.
II. 0·2181 „ 0·1541 „ AgCl.

	Found.	Theory for $C_8H_{10}N_2SCl$.
I. Cl........	17·62 per cent.	17·53 per cent.
II. Cl........	17·47 „	—

The first analysis was made with a specimen showing a primary melting point of 142—143°.

On the addition of potash or ammonia to the aqueous solution of the chloride, the free base is precipitated as a white, curdy precipitate accompanied by an odour of benzyl mercaptan. The melting point of the base, after drying over oil of vitriol, is given by Bernthsen and Klinger at 71—72°, but here again these chemists must have been using impure material, as the following experiments show.

A quantity of the base was precipitated from a moderately strong aqueous solution of the chloride by the addition of a little *less* than the calculated amount of potassium hydroxide in normal solution; the precipitate, after washing and draining on the filter pump, was dissolved in the minimum quantity of strong alcohol by very gentle warming, and to the clear, cold solution, water was added until a permanent opalescence set in; after standing over night, a quantity of ill-defined, thin, glistening prisms had separated, whilst the whole smelt strongly of benzyl mercaptan. The crystals were collected, washed, and pressed between folds of bibulous paper, the drying being completed by exposure over oil of vitriol for several days.

The product, thus obtained, was found on analysis to contain only 2·01 per cent. of nitrogen (theory 16·86), while the sulphur amounted to 22·7 per cent. (theory 19·27); it was, therefore, a very impure product, yet, strange to say, its melting point was exactly 71—72°, that is, identical with the temperature given by the above chemists as the melting point of the pure base.

It is evident from the foregoing that the free base is a very unstable substance, yet the results just recorded were mainly due to a weak point in the method of preparation, namely, the employment of too strong solutions during precipitation, whereby the base is momentarily exposed to the contact of free alkali, to the decomposing action of which it is very sensitive. By avoiding this I have obtained a very pure specimen of the base in the following simple manner.

To a *one per cent.* solution of the chloride, somewhat less than the required amount of normal potassium hydroxide is added drop by drop, with constant agitation; the base is slowly precipitated in fine, snow-white flocks, seen under the microscope to consist of minute interlacing needles; the precipitate is quickly thrown on a filter, washed thoroughly, drained, and after pressure between folds of bibulous paper, dried over oil of vitriol for several days. It forms a very light, white, microcrystalline powder, which melts at 88°, and then almost immediately decomposes.*

A specimen prepared as above afforded the data as follows:—

I. 0·1648 gram gave 23·9 c.c. nitrogen at 15° and 755 mm.
II. 0·2442 „ 0·1386 gram H_2O and 0·5086 gram CO_2.
III. 0·2205 „ by Carius' method, followed by fusion with potassium nitrate, 0·3116 gram $BaSO_4$.

	Theory for $C_8H_{10}N_4S$.	Found.
C..........	57·83 per cent.	57·92 per cent.
H..........	6·02 „	6·31 „
N..........	16·86 „	16·78 „
S..........	19·27 „	19·41 „

The base is freely soluble in chloroform, benzene, ether, and alcohol, also in carbon bisulphide, which easily acts upon it. It is metameric with monobenzylthiocarbamide, m. p. 101°. The platinochloride is precipitated in golden-yellow, microscopic prisms on the addition of chloroplatinic acid to a moderately strong solution of the chloride.

---

* Bernthsen and Klinger remarked how easily this compound decomposes into dicyandiamide and benzyl mercaptan, yet they give no analytical data for their base.

Dried at 100° C., it has the composition $(C_8H_{10}N_2S)_2,H_2PtCl_6$.

	Theory.	Found.
Pt	26·21 per cent.	26·36 per cent.

It melts at 157° with violent decomposition, it is sparingly soluble in cold water, and although it easily dissolves in the boiling liquid, it is quickly decomposed with separation of benzyl chloride and precipitation of a dark-brown, amorphous compound rich in platinum. This concludes the repetition of Bernthsen and Klinger's work, with the so-called benzylimidothiocarbamate hydrochloride.

The addition of auric chloride to the artificially-cooled aqueous solution of the compound precipitates the chloraurate in brilliant, golden-yellow spangles having the composition $C_8H_{10}N_2S,HAuCl_4$.

0·1965 gram gave on ignition 0·077 gram of gold.

	Theory for above.	Found.
Au	38·83 per cent.	39·18 per cent.

It melts with decomposition at 130—131°; and in presence of water it is easily broken up by gentle warming with separation of gold in glistening spicules.

The neutral sulphate is precipitated in the crystalline form, after a short time, on adding sulphuric acid in excess to a strong aqueous solution of the chloride. It is very freely soluble in water and in alcohol; from the latter it separates by spontaneous evaporation in thick, glassy, six-sided prisms which melt at 132—133°. They have the composition $(C_8H_{10}N_2S)_2,H_2SO_4$ as deduced from the following determination of the sulphuric radicle.

0·2932 gram gave 0·159 gram $BaSO_4$.

	Theory.	Found.
SO_4........	22·32 per cent.	22·34 per cent.

An acid sulphate could not be obtained even under the most favourable conditions; thus the neutral sulphate crystallises very readily from dilute sulphuric acid, in which it is much less soluble than in pure water. With chromium sulphate, it yields, after several weeks' standing, crystals of an alum which are very unstable, decomposing almost completely into their constituents on attempting to recrystallise them. The alum is only formed when a large excess of chromium sulphate is present.

The picrate, which is almost insoluble in cold water, separates from its hot solution in small, golden-yellow needles which melt at 182—183°. These have the composition $C_8H_{10}N_2S,C_6H_2(NO_2)_3{\cdot}OH$.

0·223 gram gave 33·8 c.c. nitrogen at 18° and 762·5 mm.

or N .... 17·48 p. c. Theory. N.... 17·72 p. c.

By the addition of mercuric chloride to a hot aqueous solution of the chloride of this base, a very characteristic mercurochloride is formed; it separates from the boiling solution on slowly cooling in beautiful, thin, white, lustrous prisms, which are easily obtained upwards of 3 inches in length.

As deduced from the following analytical data, these crystals have the composition $C_8H_{10}N_2S,HCl,HgCl_2$.

0·494 gram gave 0·243 gram HgS.
0·317 „ 0·286 „ AgCl.

	Theory for above.	Found.
Hg..........	42·23 per cent.	42·40 per cent.
Cl..........	22·49 „	22·30 „

The compound melts at 112°, is moderately soluble in cold water and alcohol, easily in boiling water. Alkalis produce a white precipitate in its solutions, which is not redissolved again by the addition of acids. The behaviour of this mercurochloride on heating and its decomposition by alkalis are reactions which deserve special attention, for they afford valuable information bearing on the constitution of this particular class of thiocarbamide-derivatives. I have therefore studied these decompositions in some detail, the results of which I shall now proceed to describe.

Action of Potassium Hydroxide on $C_8H_{10}N_2S,HCl,HgCl_2$.

As mentioned above, potassium hydroxide produces in the solutions of this substance a bulky, snow-white precipitate; between two and a half and three molecular proportions of alkali are required for the complete precipitation of one molecular proportion of the mercurochloride. This white precipitate is the already known compound $HgCl{\cdot}SC_7H_7$.

Analytical data:

0·419 gram gave 0·165 gram AgCl.
0·4904 „ by distillation with $PbCrO_4$, and CaO in front of tube, 0·275 gram Hg.

	Theory for $HgCl{\cdot}SC_7H_7$.	Found.
Hg..........	55·78 per cent.	56·08 per cent.
Cl..........	9·90 „	9·73 „

The filtrate from this compound gives with ammonio-silver nitrate a bright-yellow precipitate, with ammonio-copper sulphate a black precipitate, reactions characteristic of *cyanamide*. A specimen of the copper precipitate collected and dried contained Cu = 60·72 per cent.

Theory for $CuN{\cdot}CN$ = 61·16 per cent. The decomposition of the mercurochloride by alkali takes place therefore in accordance with the equation:—

$$C_8H_{10}N_2S,HCl,HgCl_2 + 2KOH = HgCl{\cdot}SC_7H_7 + CN{\cdot}NH_2 + 2KCl + 2H_2O,$$

the correctness of which is proved by the following quantitative experiment:—

9·46 grams of the chloride (1 mol.) were decomposed by a slight excess of alkali, filtered directly into ammoniacal copper sulphate solution, whereby the cyanamide was immediately fixed as $CuN{\cdot}CN$; from this quantity the weights of each precipitate obtained were:

		Theory.
$HgCl{\cdot}SC_7H_7$	6·8 grams	7·16 grams.
$CuN{\cdot}CN$..........	2·0 „	2·06 „

The fact that, in practice, nearly 3 mols. of alkali are required to realise the above decomposition, is no doubt due to the acidic properties exhibited by cyanamide.

Action of Heat on the Compound $C_8H_{10}N_2S,HCl,HgCl_2$.

The following observations were made during a determination of the melting point of this substance. At 112° it melted to a perfectly clear liquid; but on raising the temperature to 138°,[*] evolution of gas (hydrogen chloride) commenced; at 159°, while gas continued to be freely evolved, the liquid became turbid; at 185° it thickened, and at 193° was almost solid again, while the evolution of gas had ceased; the solid melted again, with blackening, above 200°; as the evolution of gas ceased, a slight odour of benzyl chloride was recognisable.

A quantity of the substance was therefore spread in a thin layer over the bottom of a conical flask, and heated until the odour of benzyl chloride was noticeable; it was found that almost exactly 1 mol. of hydrogen chloride had been eliminated. To be certain of the homogeneous character of the residue, the latter, when cold, was broken up and extracted with boiling alcohol and boiling water in turn. When dried in the water-oven, and subsequently over oil of vitriol, it formed a pale-buff coloured, amorphous substance, which afforded the following numbers on analysis:—

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[*] It will be noted that this temperature is 36° lower than even the melting point of the original chloride, $C_8H_{10}N_2S,HCl$.

I. 0·3276 gram gave 0·2165 gram AgCl.
II. 0·6676 „ 35·2 c.c. of nitrogen at 18° and 760·5 mm.
III. 0·4856 „ by distillation with $PbCrO_4$,* and layer of CaO in the front part of tube, 0·2232 gram Hg.

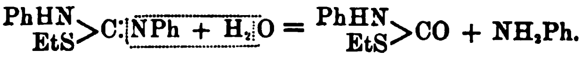
	Theory for $C_8H_{10}N_2S,HgCl_2$.	Found.
Cl	16·24 per cent.	16·34 per cent.
N	6·40 „	6·05 „
Hg..........	45·76 „	45·96 „

Scarcely anything had been extracted by the alcohol or water. On treating this new compound with alkalis, it is immediately decomposed with *separation of all the mercury as mercuric sulphide;* on comparing this decomposition with the behaviour of the parent mercurochloride towards alkalis, it is evident that *an alteration, at least in the position of the benzyl-group,* has taken place simultaneously with the loss of 1 mol. of hydrogen chloride. I find the formation of monomercurochlorides, having somewhat similar properties to the above, to be general for the different thiocarbamide-compounds described in the present paper, and reserve for a future communication a detailed account of the series.

Action of 20 *per cent. Sulphuric Acid at* 160—180° *on the Compound* $C_8H_{10}N_2S,HCl$.

Of the different reactions studied by Will in his investigations of the compounds derived from thiocarbanilide and ethyl iodide and ethylene dibromide respectively, there is none perhaps which lends more weight to the constitutional formulæ accepted for these compounds, than the decomposition which they undergo when heated to 160—180° with 20 per cent. sulphuric acid.

Under these conditions an "ester" of a substituted thiocarbamic acid is formed, through the interaction of water, thus:—



$$\left.\begin{matrix}\mathrm{PhHN}\\ \mathrm{EtS}\end{matrix}\right>\mathrm{C}\!:\!\boxed{\mathrm{NPh + H_2}}\mathrm{O} = \left.\begin{matrix}\mathrm{PhHN}\\ \mathrm{EtS}\end{matrix}\right>\mathrm{CO} + \mathrm{NH_2Ph}.$$

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* Distillation with CaO alone, as in the usual method, did not give satisfactory results; the distillate of Hg, besides being accompanied by oily matter, interfering with its clean separation, was in most cases devoid of lustre. By burning the substance with $PbCrO_4$, very brilliant distillates were obtained.

This decomposition (which, on the strength of Will's limited work, has been put forward in certain text-books as a generic reaction) had hitherto never been extended to the primary thiocarbamide-derivatives of this class. I have therefore put Bernthsen and Klinger's benzyl-compound to the experimental test, with the following unexpected results.*

Five grams of the pure chloride were sealed up in a glass tube with 12 c.c. of sulphuric acid of the above strength; the temperature of the mixture was quickly raised to 170°, and maintained at that for two hours. There was a considerable rush of gas (consisting principally of carbon dioxide with some hydrogen sulphide, and carbon oxysulphide probably) on opening the tube, while a comparatively large amount of a pale-reddish oil lay at the bottom of the tube. The contents were quickly transferred to a separating funnel, when, in a few moments, the oil suddenly and completely solidified to a crystalline mass having a pearly lustre. The substance, after two crystallisations from hot alcohol, was obtained quite pure in the form of small, white, feathery crystals having a fine lustre. The compound contained no nitrogen, and therefore could not be the expected benzyl thiocarbamate.

The following numbers, yielded by a specimen purified as above and dried over oil of vitriol, prove the substance to have the composition C_7H_7S or $C_{14}H_{14}S_2$:—

I. 0·2566 gram gave 0·1325 gram H_2O and 0·640 gram CO_2.
II. 0·1645 „ by Carius' method, followed by fusion with potassium nitrate, 0·3141 gram $BaSO_4$.

	Theory for $C_{14}H_{14}S_2$.	Found.
C.........	68·29 per cent.	68·02 per cent.
H.........	5·69 „	5·73 „
S.........	26·02 „	26·25 „

The substance does not admit of a vapour-density determination, as it decomposes on volatilisation; this, and its sparing solubility in cold alcohol, crystalline form, and melting point, 68·5°, point to the conclusion that it is benzyl disulphide, the melting point of this substance being given as 69—70° (Klinger), 71—72° (Hofmann). In the mother liquor from the first crystallisation, a small quantity of

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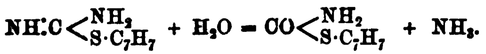
* In conformity with Will's reaction, it was to be supposed that in this case the decomposition would take place thus,



$$NH{:}C{<}{\begin{smallmatrix}NH_2\\ S\cdot C_7H_7\end{smallmatrix}} + H_2O = CO{<}{\begin{smallmatrix}NH_2\\ S\cdot C_7H_7\end{smallmatrix}} + NH_3.$$

Benzyl thiocarbamate.

benzyl mercaptan was detected. Besides a trace of the undecomposed base, nothing but ammonia was present in the aqueous portion of the tube contents.

With such a result, an obvious question naturally arises before any conclusions can be drawn: "Does the benzyl disulphide result from the direct decomposition of the original thiocarbamide-derivative, or is it merely present as a product of decomposition of the previously formed benzyl thiocarbamate?" This was only to be decided by direct experiment.

Preparation of Benzyl Thiocarbamate.

In seeking a method for the preparation of this compound, I have availed myself of an interesting reaction discovered by Pinner, in the course of his investigations on the imido-ethers. By allowing a solution of ethyl thiocyanate in absolute alcohol, after saturation with hydrogen chloride, to stand for some time, Pinner and Schaumann (*Ber.*, **14**, 1082) obtained ethyl thiocarbamate.

$$C_2H_5SCN + H_2O = NH_2{\cdot}CO{\cdot}S{\cdot}C_2H_5.$$

This reaction I have extended to benzyl thiocyanate with moderate success.

A solution of the thiocyanate* in nearly absolute alcohol was saturated with dry hydrogen chloride at a low temperature, and the mixture allowed to remain for 10 days in a sealed flask; this was opened and resealed from time to time to avoid fracture from a gradually accumulating internal pressure. The product was poured into a comparatively large volume of water, the separated crystalline precipitate, after draining on the filter-pump, was purified by crystallisation from alcohol, and subsequently from hot benzene; from this solvent the new substance separates on cooling, in beautiful, large, thin, glistening plates, of an exceptionally fine lustre. The yield is small, as before the assimilation of water by the thiocyanate is complete, the thiocarbamate commences to decompose (see Action of Dilute Sulphuric Acid on Benzyl Thiocarbamate, p. 294), evidence of which is obtained by the separation of crystals of ammonium chloride in the liquid.

I. 0·248 gram gave, by Carius' method, followed by fusion with potassium nitrate, 0·3495 gram $BaSO_4$.

II. 0·2830 gram gave 0·1475 gram H_2O and 0·598 gram CO_2.

III. 0·3076 gram gave 22·6 c.c. nitrogen at 15° C. and 761 mm.

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* The filtrate, obtained directly from the interaction of benzyl chloride and potassium thiocyanate after potassium chloride had ceased to separate, was the solution actually used.

	Theory for C_8H_9NSO.	Found.
S	19·16 per cent.	19·33 per cent.
C	57·48 „	57·62 „
H	5·38 „	5·78 „
N	8·38 „	8·55 „

The crystals, which melt at 125°, are soluble in alcohol, ether, acetone, freely in hot benzene, sparingly in the cold, and insoluble in water or petroleum. That the substance is benzyl thiocarbamate is proved by the following experiments.

Reactions and Properties of Benzyl Thiocarbamate.

When heated, the crystals melt, at the temperature above stated, to a clear liquid; at 180°, decomposition commences, followed by a separation of crystals at 186°, while the odour of benzyl mercaptan becomes evident.

Half a gram of the substance was heated in a small Würtz's distillation-flask at 200° in a current of hydrogen,* the volatile product being aspirated through an alcoholic solution of mercuric chloride; a bulky white precipitate was produced in this solution, which analysis proved to be the compound $HgCl{\cdot}S{\cdot}C_7H_7$; the crystalline residue in the flask, after washing with ether, was identified as cyanuric acid; its hot aqueous solution gave, on cooling, a fine violet crystalline precipitate with ammoniacal copper sulphate, a reaction characteristic of that acid. The decomposition by heat is represented, therefore, by the equation:—

$$NH_2{\cdot}CO{\cdot}S{\cdot}C_7H_7 = C_7H_7{\cdot}SH + HCNO,$$

the cyanic acid being polymerised at the temperature of formation. This decomposition is similar to that shown by Pinner and Schaumann to take place when ethyl thiocarbamate is heated at 150° in sealed tubes. The reaction is, therefore, in all probability, a generic one.

Silver nitrate in alcoholic solution gives, with benzyl thiocarbamate, a snow-white precipitate, which has the composition $CONH_2{\cdot}S{\cdot}C_7H_7,2AgNO_3$.

0·168 gram gave 0·1185 gram AgCl.

	Theory for above.	Found.
Ag........	53·07 per cent.	53·08 per cent.

This substance is almost insoluble in water and alcohol. When treated with ammonia solution in excess, it is converted into a yellow powder, while half the silver, accompanied by a molecular proportion of carbamide, passes into solution. The yellow substance is silver benzyl mercaptide.

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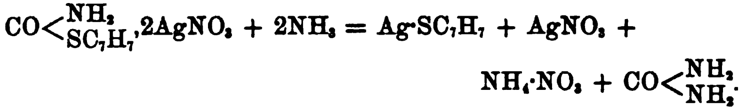
* Benzyl mercaptan easily oxidises in a current of hot air to $(C_7H_7)_2S_2$.

Ag found, 46·62 per cent. Theory for $AgSC_7H_7 = 46{\cdot}75$ per cent.

The decomposition by ammonia takes place in accordance with the equation :—



$$CO{<}^{NH_2}_{SC_7H_7},2AgNO_3 + 2NH_3 = Ag{\cdot}SC_7H_7 + AgNO_3 + NH_4{\cdot}NO_3 + CO{<}^{NH_2}_{NH_2}.$$

Silver benzyl mercaptide, prepared in this way, is a pale sulphur-yellow, amorphous powder, insoluble in the ordinary solvents.

Action of 20 *per cent. Sulphuric Acid on Benzyl Thiocarbamate at* 160—180°.

A couple of grams of the pure substance were heated in a sealed tube at 170°, under exactly the same conditions as the original thiocarbamide benzyl-derivative. The thiocarbamate was completely decomposed with formation of a dark-reddish oil, while abundance of carbon dioxide was evolved on opening the tube. The contents were poured into a small separating funnel, where the oil remained for several days *without showing any signs of solidification*, and it was easily identified as almost pure benzyl mercaptan by its conversion into $HgClS{\cdot}C_7H_7$ and $Ag{\cdot}SC_7H_7$. Nothing besides ammonia could be detected in the aqueous portion of the tube contents.

The decomposition of the benzyl thiocarbamate in the foregoing experiment is, therefore, very simple, viz. :—

$$NH_2{\cdot}CO{\cdot}\boxed{SC_7H_7 + H}OH = C_7H_7{\cdot}SH + CO_2 + NH_3.$$

and *no benzyl disulphide whatever* appears in the decomposition.

After such a sharp result, there is strong reason to conclude that the benzyl disulphide produced in the reaction already described does *not* result from the decomposition of previously formed benzyl thiocarbamate, for since both experiments were carried out under exactly similar conditions, it cannot be argued that the disulphide results from oxidation of benzyl mercaptan, itself produced from the decomposition of the thiocarbamate, according to the above equation. That the disulphide is a product of the direct decomposition of the compound $C_8H_{10}N_2S,HCl$, does not, however, appear so clear, yet the results obtained justify the following deductions :—

1. That Will's reaction (which in the subsequent pages is confirmed in the case of mono- and di-substituted thiocarbamides) does not appear to hold good for the primary thiocarbamide-derivatives* of this class.
2. The production, as principal decomposition-product, of a compound containing *at least* 2 atoms of sulphur in the molecule, argues for a higher molecular weight than the generally accepted formula, $C_8H_{10}N_2S,HCl$, indicates.

Until further evidence is obtained on this point, I refrain from giving an equation to express the decomposition, since the formation, besides the disulphide, of a small quantity of benzyl mercaptan, already noticed, may be an essential feature in the decomposition.

It is worthy of note that, unlike the substituted thiocarbamide-derivatives, a certain portion of the base escapes decomposition, even though the time and temperature be increased.

II. *Benzyl Chloride and Monophenylthiocarbamide.*

These readily combine in molecular proportion when heated for a short time in alcoholic solution on the water-bath; the product, after evaporation of the alcohol, remains as a thick syrup, which, on standing in a desiccator for several days, solidifies to a radiate crystalline mass. The compound is soluble in all proportions in water and in alcohol. It has the composition $CSN_2H_3(C_6H_5)C_7H_7Cl$, and melts at 112°; at 176°, signs of decomposition set in.

Potassium hydroxide (1 mol.) added to the aqueous solution precipitates the free base as a thick, pale-yellow oil; this solidifies, after a few hours, to a brittle mass, easily soluble in alcohol; by gradually adding water to this solution until a slight opalescence appears, a commencement of crystallisation is soon effected. In this way the new substance may be easily obtained in well-defined, colourless, flat prisms, which are quite pure after a single crystallisation.

A specimen, obtained thus, afforded the following data:—

I. 0·5029 gram gave 52 c.c. nitrogen at 20° and 766·5 mm.
II. 0·3494 „ 0·1875 gram H_2O and 0·887 gram CO_2.

	Theory for $C_1 H_{14}N_2S$.			Found.	
C........	69·42	per cent.		69·23	per cent.
H........	5·78	„		5·96	„
N........	11·57	„		11·86	„
S........	13·22	„	(by diff.)	12·95	„

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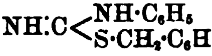
[*] See also result from allyl bromide compound.

The crystals melt at 81—82°, and give off benzyl mercaptan a few degrees higher; the base is most probably benzyl imidophenylthiocarbamate, and its constitution,  $NH{:}C{<}\begin{smallmatrix}NH\cdot C_6H_5\\ S\cdot CH_2\cdot C_6H_5\end{smallmatrix}$. It is freely soluble in alcohol, ether, and benzene, almost insoluble in water or light petroleum. It is metameric with phenylbenzylthiocarbamide (A. E. Dixon, Trans., 1889, 55, 301) melting at 153—154°.

With platinum chloride, it yields a dark-brown resinous precipitate which soon decomposes. The picrate crystallises from boiling water in fine, brilliant, golden-yellow needles which melt at 136—137°. These are almost insoluble in cold water, and have the composition $C_{14}H_{14}N_2S,C_6H_2(NO_2)_3\cdot OH$.

0·167 gram gave 21·8 c.c. of nitrogen at 18° and 760·5 mm.,

or N........ 15·00 p. c. Theory...... 14·86 p. c.

The neutral sulphate forms a thick oil, sparingly soluble in cold water. With mercuric chloride, the original chloride yields a derivative which, in aqueous or alcoholic solution, readily decomposes with elimination of hydrogen chloride, even below the temperature of the water-bath.

This compound, which from a single chlorine determination appears to have the composition $C_{14}H_{14}N_2S,HCl,HgCl_2$, forms short prisms which in the dry state melt at 128—129° to a milky liquid; at 140° gas (hydrogen chloride) commences to be evolved, the evolution becoming very violent at 155° and upwards.

Action of 20 *per cent. Sulphuric Acid on the Compound* $C_{14}H_{14}N_2S,HCl$.

Eight grams were heated for two hours at 170—180°, as in the previous experiments. All the chloride was decomposed with separation of an ill-defined crystalline mass, but *there was no appreciable evolution of gas on opening the tube.* The crystalline product was purified by pressure between folds of bibulous paper, and crystallisation from benzene; it was finally obtained in the form of hard, glassy, oblique prisms, by gradual precipitation of the benzene solution with light petroleum.

Analytical data—

I. 0·2026 gram gave 0·1026 gram H_2O and 0·5125 gram CO_2.
II. 0·2284 „ 11·50 c.c. of nitrogen at 13° and 753 mm.
III. 0·1408 „ 0·136 gram $BaSO_4$, by Carius' method.

	Theory for $C_{14}H_{13}NSO$.		Found.	
C........	69·13 per cent.		68·98 per cent.	
H	5·35 ,,		5·62 ,,	
N	5·76 ,,		5·86 ,,	
S........	13·16 ,,		13·27 ,,	
O........	6·58 ,,	(by diff.)	6·27 ,,	

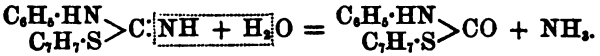
The crystals melt at 96—97°, and when heated to 200° in a sealed tube only a trace of benzyl mercaptan is formed; when rapidly heated on platinum foil, the irritating odour of phenyl isocyanate is easily recognised. The compound is easily soluble in alcohol and ether, insoluble in water or light petroleum.

With silver nitrate, the alcoholic solution gives a bulky, white precipitate which has the composition $C_{14}H_{13}NSO,2AgNO_3$.

0·2515 gram ignited in hydrogen gave 0·092 gram Ag.

	Theory for above.	Found.
Ag..........	37·05 per cent.	36·58 per cent.

When heated with alcoholic solution of ammonia, silver benzyl mercaptide is formed, while half the silver, together with carbanilamide, pass into solution. This decomposition proves the original compound to be the expected benzyl phenylthiocarbamate formed, together with ammonia (this was identified in the aqueous portion of the tube contents), according to Will's equation :—



$$\genfrac{}{}{0pt}{}{C_6H_5\cdot HN}{C_7H_7\cdot S}\!>\!C\boxed{NH + H_2}O = \genfrac{}{}{0pt}{}{C_6H_5\cdot HN}{C_7H_7\cdot S}\!>\!CO + NH_3.$$

The property of combining directly with 2 mols. of silver nitrate appears to be characteristic of the thiocarbamic "esters."

III. *Benzyl Chloride and Diphenylthiocarbamide.*

The product from the interaction of the above in presence of alcohol forms, after purification, small, brilliant, vitreous prisms which have the composition $C_{20}H_{19}N_2SCl$. They melt at 152—153°, are freely soluble in alcohol, almost insoluble in water, while, strangely, they melt in boiling water without sensibly dissolving.

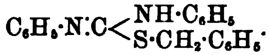
The free base, produced by the action of alkali on the alcoholic solution of the chloride and precipitation of the whole with water, forms a clear, pale-yellow, very viscid oil, which exhibits no signs of crystallisation after standing for several weeks over oil of vitriol. It is freely soluble in alcohol, ether, and benzene, but almost insoluble in water.

A specimen (purified as far as possible) gave the following data :—

I. 0·179 gram gave 13·7 c.c. of nitrogen at 15° and 765 mm.
II. 0·212 „ by Carius' method, followed by fusion with potassium nitrate, 0·149 gram $BaSO_4$.

	Theory for $C_{20}H_{18}N_2S$.	Found.
N	8·80 per cent.	8·97 per cent.
S	10·06 „	9·62 „

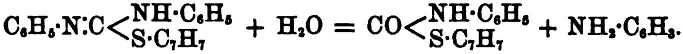
This base is most probably benzyl phenylimidophenylthiocarbamate and its constitution



$C_6H_5\cdot N{:}C<^{NH\cdot C_6H_5}_{S\cdot CH_2\cdot C_6H_5}$.

It is a thin liquid at the temperature of the water-bath, and this, when poured into ice-cold water, forms a mass resembling plastic sulphur in consistency. It is freely soluble in alcohol, ether, chloroform, and benzene. The metameric thiocarbamide which I have quite recently obtained melts at 103°, and shall be described shortly in another communication.

The above base, when heated with 20 per cent. sulphuric acid in a sealed tube at 170°, decomposes in a manner similar to the monophenyl-derivative, aniline being formed as the secondary product, thus:—



$$C_6H_5\cdot N{:}C<^{NH\cdot C_6H_5}_{S\cdot C_7H_7} + H_2O = CO<^{NH\cdot C_6H_5}_{S\cdot C_7H_7} + NH_2\cdot C_6H_5.$$

This decomposition points to the above constitution.

The picrate precipitated from its alcoholic solution by water forms, after drying, an orange-yellow mass, which does not appear to be a definite compound. A mercurochloride was prepared in the form of small, heavy, white prisms having the composition $C_{20}H_{19}N_2SCl,HgCl_2$.

Analytical data—

I. 0·2344 gram gave 0·16 gram AgCl.
II. 0·335 gram distilled with $PbCrO_4$, and a layer of CaO in front, gave 0·1065 gram Hg.

	Theory for above.	Found.
Cl	17·02 per cent.	16·87 per cent.
Hg	32·00 „	31·79 „

Whilst the compound easily decomposes in presence of alcohol, losing hydrogen chloride, the crystals melt at 136° to an opalescent liquid from which gas (hydrogen chloride) commences to be evolved at 160°.

IV. *Allyl Bromide and Thiocarbamide.*

These, when dissolved in alcohol in molecular proportion, interact readily on the application of a gentle heat, and combination is complete after a few minutes' boiling. The product separates by slow evaporation of the alcoholic solution in lanceolate combinations of large, flat, oblique prisms very freely soluble in water and alcohol.

They have the composition $C_4H_9N_2SBr$.

0·5125 gram gave 0·4825 gram AgBr = Br 40·38 per cent. Theory for above = 40·60 per cent.

The substance melts at 84—85°; it is very deliquescent, and easily forms supersaturated solutions both in water and alcohol; it is insoluble in ether, chloroform, and benzene.

The free base, which is easily soluble in water, could not be isolated in the pure state on account of the extreme ease with which it decomposes into allyl mercaptan and cyanamide. The freshly-prepared aqueous solution obtained by the addition of alkali to the bromide, when shaken with ether yields the greater part of the base to the latter solvent; such a solution when evaporated in a rapid current of air yields a residue which, in spite of the low temperature attained, is little better than a mixture of the mercaptan and cyanamide, both of which can be easily separated and identified. From the residue left on evaporation of the aqueous solution (residue from ethereal extract), a small quantity of allylthiocarbamide (m. p. 78°) was extracted. A tendency to revert to the metameric and more stable thiocarbamide was not noticed in any of the other bases described in this paper, and in the present case it is most probably due to a recombination of liberated mercaptan and cyanamide. The salts of this base, on the other hand, are well defined and very characteristic. The sulphate, produced by action of sulphuric acid or silver sulphate on the bromide, crystallises from water in clusters of large, needle-like prisms having a silky lustre.

These have the composition $(C_4H_8N_2S)_2SO_4$.

0·316 gram gave 0·224 gram $BaSO_4$, or SO_4 = 29·20 per cent. Theory = 29·09 per cent.

The solution, mixed with chromium sulphate and allowed to remain for several weeks, yields fine crystals of an alum: the yield, however, is comparatively small. Its formation cannot be hastened, but when once produced it is fairly stable, and may be crystallised from a solution of chromium sulphate in an almost pure state,* as the following analytical results show.

---

* It partly decomposes when crystallised from pure water.

The crystals, which resemble ordinary chrome alum, have the composition $(C_4H_9N_2S)_2Cr_2(SO_4)_4,24H_2O$.

I. 0·3013 gram at 120° C. lost 0·1135 gram H_2O.
II. 0·3013 gram gave 0·040 gram Cr_2O_3.
III. 0·2256 „ 0·186 gram $BaSO_4$.

	Found.	Theory for above.
H_2O	37·67 per cent.	37·43 per cent.
Cr	9·11 „	9·01 „
SO_4	34·00 „	33·27 „

The numbers obtained point to the presence of a slight excess of chromium sulphate in the crystals.

With picric acid, the allyl base yields a very characteristic compound which crystallises from the hot aqueous solution in large, orange-yellow, highly refracting prisms; these are easily obtained from two to three inches long. They melt at 141—142°, and have the composition $C_4H_8N_2S,C_6H_2(NO_2)_3{\cdot}OH$.

0·172 gram gave 29·8 c.c. nitrogen gas at 14° and 756·5 mm.,

or N = 20·18 per cent. Theory = 20·38 per cent.

The chloride, $C_4H_9N_2SCl$, prepared from allyl chloride and thiocarbamide, resembles the bromide, and melts at 91—92°. With platinum chloride, it yields an orange-red platinochloride, which, however, is a decomposition-product. With mercuric chloride, a derivative is obtained which, in solution, easily decomposes yielding a crystalline precipitate of a mercurial derivative, decomposing with formation of sulphide by action of alkali.

Action of 20 *per cent. Sulphuric Acid on the Compound* $C_4H_9N_2SBr$.

When heated for a couple of hours at 160°, as in the previous experiments, this compound yields as a decomposition-product a dark-brown oil, while carbon dioxide, with a trace of sulphuretted gases, is evolved on opening the tube. The oil was taken up with ether, and the solution, dried over calcium chloride, was distilled, as far as possible, on the water-bath. The residual, clear-brown oil was finally dried for several days over oil of vitriol in a vacuum. It has a most disagreeable and persistent fetid odour which is quite distinct from that of allyl mercaptan, and in the very dilute state bears some resemblance to the odour of mushrooms. The quantity of material at my disposal was small, and, being concerned for the present merely with the identification of the substance, I have not attempted any further purification of the oil. The odour also renders it a very disagreeable substance to work with.

The properties of the oil exclude the presence of any allyl mercaptan, viz.:—

1. With mercuric chloride, a faint, cloudy precipitate, which blackens on heating.
2. The oil is not freely soluble in cold alcohol.
3. It may be heated to 100° without much volatilisation (C_3H_5·SH boils at 90°).

The absence of the mercaptan being proved, the subjoined analytical data, though not very satisfactory, leave little doubt that the oil obtained as above is an impure specimen of the hitherto undescribed allyl disulphide.

I. 0·1942 gram burnt with $PbCrO_4$ gave 0·119 gram H_2O and 0·321 gram CO_2.
II. 0·2596 gram gave 0·166 gram H_2O and 0·435 gram CO_2.
III. 0·1954 „ by Carius' method, followed by fusion with potassium nitrate, 0·584 gram $BaSO_4$.

	Theory for $(C_3H_5)_2S_2$.	Found.		
		I.	II.	III.
C	49·31 per cent.	45·07	45·69	—
H	6·84 „	6·80	7·01	—
S	43·83 „	—	—	41·08

In the second analysis, the oil had been previously heated for some time at 100°, and cooled in a vacuum. It was found to contain, in addition to the above, 1·92 per cent. of nitrogen. Though the result is not so satisfactory, it is on the whole in harmony with that of the benzyl-derivative, and favours the conclusions deduced therefrom.

V. *Allyl Bromide and Monophenylthiocarbamide.*

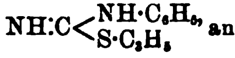
Interaction readily takes place in alcoholic solution, and is complete after a few minutes' boiling. The product, after evaporation of the solvent, is a viscid liquid which does not crystallise. When the substances act in the absence of any solvent, combination takes place quietly, and if any excess of either over the molecular proportion be used, it remains unchanged. At the ordinary temperature, the compound $C_{10}H_{13}N_2SBr$ is a remarkably viscid liquid, of a pale yellow colour, and requires several days to regain its level when placed in a horizontal position; at the temperature of the water-bath it has the consistency of a thin syrup. It is freely soluble in water and alcohol, insoluble in benzene or ether.

The free base is precipitated as a thick oil, on the addition of alkali to the aqueous solution of the bromide; the ease with which it decomposes, with liberation of allyl mercaptan, has prevented me from obtaining the base in a pure state, notwithstanding the precautions taken in the following method of procedure. To the aqueous solution of the bromide, containing pieces of ice, a little less than the required amount of alkali was slowly added with constant agitation. The precipitated oil was removed by ether, and the solution, dried by rapid shaking with anhydrous copper sulphate,* was evaporated as far as possible in a current of dry air. The residual oil, which smelt of allyl mercaptan, was finally dried over oil of vitriol for a short time under reduced pressure. As the analyses show, there was slight decomposition, with loss of the mercaptan, thereby giving a residue richer in nitrogen and poorer in sulphur than the pure base.

Data:

I. 0·1825 gram gave 24·8 c.c. of nitrogen at 13° and 753·5 mm.
II. 0·2135 „ by Carius' method 0·242 gram $BaSO_4$.

	Theory for $C_{10}H_{12}N_2S$.	Found.
N........	14·58 per cent.	15·82 per cent.
S........	16·66 „	15·58 „

These numbers correspond to a product containing between 92 and 93 per cent of the pure base. The substance analysed was a clear, golden-yellow oil, freely soluble in alcohol, ether, benzene, and chloroform. On gentle heating, it decomposes freely into allyl mercaptan and phenyl cyanamide. The base is therefore most probably allyl imidophenylthiocarbamate,  $NH{:}C{<}\begin{smallmatrix}NH\cdot C_6H_5\\ S\cdot C_3H_5\end{smallmatrix}$, and is metameric with allylphenylthiocarbamide, m.p. 98°.

The picrate separates from its hot aqueous solution in rosettes of microscopic needles of a pale sulphur-yellow colour; they melt at 133°.

When heated with 20 per cent. sulphuric acid, this base yields, besides ammonia, a foul smelling oil, while there is evolution of carbon dioxide on opening the tube. I have not attempted to purify the oil, as a detailed study of these allyl-derivatives is not desirable at present, my purpose being sufficiently served with the examination of the benzyl-derivatives. I may add, however, that from the behaviour of the crude oil towards silver nitrate, I have little doubt as to its being a mixture of $CONHC_6H_5{\cdot}S{\cdot}C_3H_5$ and $C_3H_5{\cdot}SH$, the latter arising from decomposition of the thiocarbamate. The presence of the carbon dioxide also points to this.

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* This was found to be the best substance for the purpose: calcium chloride is too slow in its action, and an alkali effects immediate decomposition.

VI. *Allyl Bromide and Diphenylthiocarbamide.*

These substances require half an hour's boiling in alcoholic solution, before the action is complete. The new product crystallises readily from the solution in small, colourless, truncated prisms, which are easily purified by a single crystallisation.

They melt at 170—171° with decomposition, and have the composition $C_{16}H_{17}N_2S{\cdot}Br$.

0·2292 gram gave 0·1225 gram Ag Br, or Br = 22·86 per cent.

Theory for above = 22·92 per cent.

The compound is freely soluble in hot alcohol, much less so in the cold, and almost insoluble in water.

The free base, which in this case is comparatively stable, is precipitated as a thin, nearly colourless oil, when an alcoholic solution of the bromide, mixed with alkali, is poured into cold water. A quantity, separated and treated in the same manner as the previous allyl-compound, was finally obtained as a clear, pale-yellow oil, which, after a night's exposure over oil of vitriol in a vacuum, completely solidified to a hard, feathery, crystalline mass, perfectly free from the odour of allyl mercaptan.

By solution in alcohol and careful precipitation by water, the base may be obtained in very thin, six-sided plates.

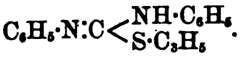
These have the composition $C_{16}H_{16}N_2S$, and melt at 57—58°, giving off allyl mercaptan a few degrees higher.

Analytical data:

I. 0·248 gram gave 22·6 c.c. of nitrogen at 13° C. and 767·5 mm.
II. 0·2139 „ 0·118 gram H_2O and 0·559 gram CO_2.
III. 0·1195 „ by Carius' method 0·105 gram $BaSO_4$.

	Theory for $C_{16}H_{16}N_2S$.	Found.
N........	10·44 per cent.	10·82 per cent.
C........	71·64 „	71·27 „
H........	5·97 „	6·12 „
S........	11·94 „	12·07 „

The compound is freely soluble in alcohol, ether, and chloroform, almost insoluble in water; when heated above its melting point, it quickly decomposes evolving allyl mercaptan, and at 130—140° a residue is obtained, having all the properties of carbo-diphenylimide. The base is most probably allyl phenylimidophenylthiocarbamate



$C_6H_5\cdot N\!:\!C\!<\!\begin{array}{l}NH\cdot C_6H_5\\ S\cdot C_3H_5\end{array}$. Its metameric thiocarbamide does not appear to have been yet described.

The chloride, $C_{16}H_{17}N_2SCl$, from allyl chloride and thiocarbanilide, forms crystals melting at 126—127°.

The picrate is an oil, almost insoluble in water; with mercuric chloride, a derivative is obtained which easily undergoes change. Like the previous base, this compound when heated with dilute sulphuric acid yields a foul-smelling oil containing allyl mercaptan.

The three allyl-derivatives just described all combine directly with bromine and chlorine, which proves that the unsaturated character of the allyl-group has remained intact during the interactions.

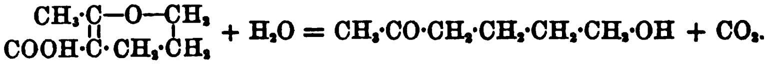
Before concluding, I wish to add that the present paper must be considered only as the first part of an investigation as yet incomplete; I therefore refrain from drawing any conclusions as regards the bearing of the results upon the constitution of thiocarbamide and its derivatives, until I have studied the action of the alkylogens on the other phenylated homologues, and completed the examination of the mercurochlorides.

University Laboratory,
Trinity College, Dublin.

XXII.—*Derivatives of Phenylhexamethylene.*[*]

By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, Jun., Ph.D.

In a paper published some time since (Trans., 1887, 51, 717), it was shown that methyldehydrohexonecarboxylic acid, when boiled with water, is converted into acetobutyl alcohol and carbonic anhydride, thus:—



$$\begin{array}{l} CH_3\cdot C\text{—}O\text{—}CH_2 \\ \quad\;\, \| \qquad\quad\;\; | \\ COOH\cdot C\cdot CH_2\cdot CH_2 \end{array} + H_2O = CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + CO_2.$$

In studying the action of water on phenyldehydrohexonecarboxylic acid (*loc. cit.*, p. 733), a similar change was found to take place, the acid decomposing into benzoylbutyl alcohol,

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

and carbonic anhydride.

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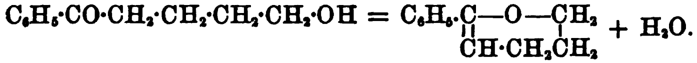
[*] *Cf.*, *Chem. Soc. Proceedings*, 1889, 161.

The two analogously constituted alcohols thus obtained exhibit a most remarkable difference in point of stability. Acetobutyl alcohol boils with only very slight decomposition at 226—227°, whereas benzoylbutyl alcohol, when only gently warmed, is decomposed at once into phenyldehydrohexone and water, thus:—



$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH = C_6H_5\cdot\begin{array}{l}C—O—CH_2\\ \|\qquad\quad |\\ CH\cdot CH_2CH_2\end{array} + H_2O.$$

The tendency of this alcohol to undergo internal condensation is so great, that when the crystalline substance is placed over sulphuric acid, the crystals are soon converted into a colourless oil, which on investigation was found to consist of pure phenyldehydrohexone. This remarkable behaviour, and the fact that benzoylbutyl alcohol had only been obtained in very small quantities, and therefore very imperfectly examined, made it advisable to repeat the experiments with larger quantities, in order to study the points of resemblance and difference between this alcohol and acetobutyl alcohol.

A considerable quantity of phenyl dehydrohexonecarboxylic acid was therefore prepared, dissolved in ammonia, reprecipitated by a dilute acid, and the resulting finely-divided substance boiled with a large quantity of water for some hours on a reflux apparatus. As soon as the evolution of carbonic anhydride had ceased, the flask was put on one side, and allowed to cool slowly.

The solution, which soon becomes turbid, deposits a considerable quantity of the benzoylbutyl alcohol in oily drops, which solidify on cooling; but in some cases the liquid becomes filled with large, transparent, leafy crystals. These beautiful crystals melt at 40—41°, and do not change when kept for months under ordinary conditions; but if a crystal is placed over sulphuric acid in a desiccator, in the course of half-an-hour, and often in a very few minutes, it entirely disappears, leaving an oily residue of pure phenyldehydrohexone. The same change naturally takes place when the crystals are heated, but boiling with water seems to have little effect on them.

Benzoylbutyl alcohol and hydroxylamine combine readily, yielding a crystalline oxime, $C_6H_5\cdot C(NOH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH$, melting at 56—57°.

Sodium amalgam converts it into phenylpentamethylene glycol:—

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH + H_2 = C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH.$$

This glycol crystallises in needles which melt at about 54°; it is far more stable than benzoylbutyl alcohol, and may be kept over sulphuric acid under reduced pressure for apparently any length of time without change.

This behaviour is in accordance with previous observations, as it has been found that the ketone alcohols are invariably less stable than the glycols obtained from them by reduction.

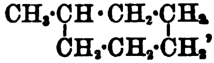
The preparation of phenylpentamethylene dibromide,

$$C_6H_5{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br,$$

from the glycol was found to be a rather difficult matter, because when the glycol is treated with a fuming solution of hydrogen bromide, the monobromide which is first formed is so insoluble that very little further action takes place, except at temperatures so high that the resulting dibromide suffers decomposition.

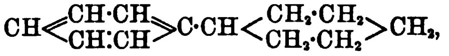
Pure phenylpentamethylene dibromide was, however, ultimately prepared by the action of phosphorus pentabromide on the chloroform solution of the glycol. It is a thick, almost colourless oil, which on standing becomes slightly yellowish.

In a previous communication, by P. C. Freer and one of us (Trans., 1888, **53**, 202), it was shown that when ethyl sodiomalonate or ethyl sodioacetoacetate is treated with methylpentamethylene dibromide, derivatives of methylhexamethylene,



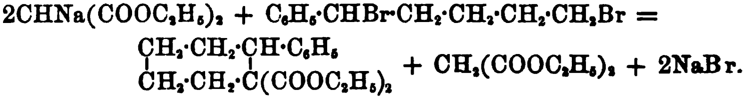
$\begin{array}{l} CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2 \\ \phantom{CH_3{\cdot}}CH_2{\cdot}CH_2{\cdot}CH_2 \end{array}$,

are formed. It appeared very interesting to determine whether analogous derivatives of phenylhexamethylene (hexahydrodiphenyl),



$CH{<}{\begin{array}{l}CH{\cdot}CH\\CH{:}CH\end{array}}{>}C{\cdot}CH{<}{\begin{array}{l}CH_2{\cdot}CH_2\\CH_2{\cdot}CH_2\end{array}}{>}CH_2$, could be obtained in like manner from phenylpentamethylene bromide. The experiments instituted with this object are, briefly described, the following:—

Ethyl malonate (2 mols.), sodium ethoxide (2 mols.), and phenylpentamethylene dibromide (1 mol.) were digested together in alcoholic solution for some time. An action sets in readily, and a thick, yellow oil is formed, which, as shown by its behaviour on hydrolysis, undoubtedly contains ethyl phenylhexamethylenedicarboxylate (2 : 1 : 1).

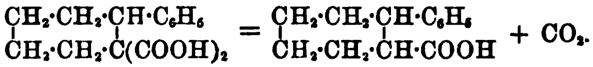


$$2CHNa(COOC_2H_5)_2 + C_6H_5{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br =$$

$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5 \\ CH_2{\cdot}CH_2{\cdot}C(COOC_2H_5)_2 \end{array} + CH_2(COOC_2H_5)_2 + 2NaBr.$$

Ethyl phenylhexamethylenedicarboxylate.

On hydrolysis, this ethereal salt yields the dicarboxylic acid, which, when heated at 160°, is resolved into carbonic anhydride and phenylhexamethylenecarboxylic acid (2 : 1).



$$\begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5 \\ CH_2{\cdot}CH_2{\cdot}C(COOH)_2 \end{array} = \begin{array}{l} CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5 \\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}COOH \end{array} + CO_2.$$

Phenylhexamethylenedicarboxylic acid (2 : 1 : 1). Phenylhexamethylenemonocarboxylic acid (2 : 1).

During this operation the liquid gets darker and darker, owing to partial decomposition, and the resulting dark-brown oily acid is extremely difficult to purify; it was, however, obtained in a pure condition by conversion, first into the barium salt, and then into the crystalline ammonium salt, which was subsequently decomposed with dilute sulphuric acid.

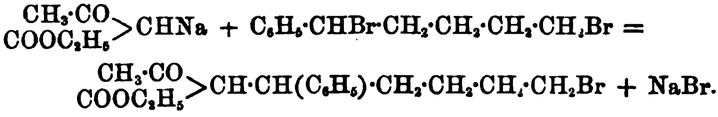
Phenylhexamethylenemonocarboxylic acid crystallises from light petroleum in compact, well-defined prisms which melt at 104—105°. Its solution in carbonate of soda does not decolorise potassium permanganate, even when allowed to stand for some time. This behaviour shows that this acid is a saturated compound (compare von Baeyer, *Annalen*, **245**, 147), and it must therefore have the constitution assigned to it above.

In studying the action of methylpentamethylene dibromide on ethyl sodiomalonate and ethyl sodioacetoacetate, it was found that hexamethylene-derivatives are formed in both cases (Freer and Perkin, Trans., 1888, **53**, 204. Compare "Action of Trimethylene Bromide on Ethyl Sodioacetoacetate," Trans., 1887, **51**, 709).

It appeared probable, therefore, that if ethyl acetoacetate was substituted for ethyl malonate, the crude product would, on hydrolysis, yield phenylhexamethylenecarboxylic acid. Our experiments in this direction have fully borne out these expectations.

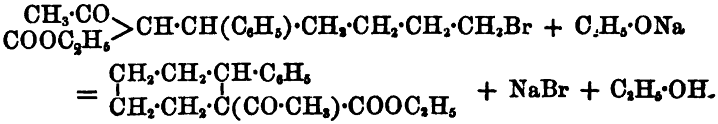
Phenylpentamethylene dibromide and ethyl sodioacetoacetate react readily, when warmed together in alcoholic solution, with formation of a yellowish oil, which, as is seen from its decomposition on hydrolysis, is evidently ethyl acetylphenylhexamethylenecarboxylate (1 : 2 : 1).

I.



$$\left.\begin{matrix}CH_3{\cdot}CO\\COOC_2H_5\end{matrix}\right>CHNa + C_6H_5{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br = \left.\begin{matrix}CH_3{\cdot}CO\\COOC_2H_5\end{matrix}\right>CH{\cdot}CH(C_6H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + NaBr.$$

II.

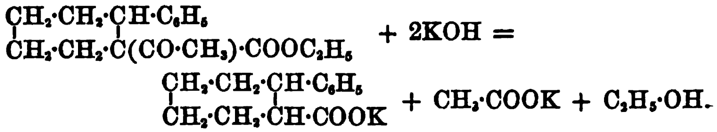


$$\left.\begin{matrix}CH_3{\cdot}CO\\COOC_2H_5\end{matrix}\right>CH{\cdot}CH(C_6H_5){\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2Br + C_2H_5{\cdot}ONa = \begin{matrix}CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5\\ | \qquad\quad | \\ CH_2{\cdot}CH_2{\cdot}C(CO{\cdot}CH_3){\cdot}COOC_2H_5\end{matrix} + NaBr + C_2H_5{\cdot}OH.$$

Ethylic acetylphenylhexamethylenecarboxylate (1 : 2 : 1).

On hydrolysis, the crude ethereal salt yields phenylhexamethylenecarboxylic acid and phenylhexamethylene methyl ketone, thus:—

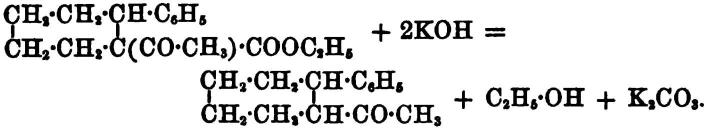
I.



$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5\\ \vert \qquad\qquad \vert\\ CH_2{\cdot}CH_2{\cdot}C(CO{\cdot}CH_3){\cdot}COOC_2H_5\end{array} + 2KOH = \begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5\\ \vert \qquad\qquad \vert\\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}COOK\end{array} + CH_3{\cdot}COOK + C_2H_5{\cdot}OH.$$

Potassium phenylhexamethylene-carboxylate (2 : 1).

II.



$$\begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5\\ \vert \qquad\qquad \vert\\ CH_2{\cdot}CH_2{\cdot}C(CO{\cdot}CH_3){\cdot}COOC_2H_5\end{array} + 2KOH = \begin{array}{l}CH_2{\cdot}CH_2{\cdot}CH{\cdot}C_6H_5\\ \vert \qquad\qquad \vert\\ CH_2{\cdot}CH_2{\cdot}CH{\cdot}CO{\cdot}CH_3\end{array} + C_2H_5{\cdot}OH + K_2CO_3.$$

Phenylhexamethylene methyl ketone (2 : 1).

The phenylhexamethylenecarboxylic acid obtained by this method is rather easier to purify than that formed by the decomposition of the dicarboxylic acid. A careful comparison of the two products has shown that they are identical.

Phenylhexamethylene methyl ketone is produced in small quantity by the hydrolysis of ethylic acetylphenylhexamethylenecarboxylate with potassium hydrate; it crystallises in needles which melt at about 78—79°. It combines readily with hydroxylamine forming a syrupy hydroxime, which was not obtained in a crystalline condition.

Phenyldehydrohexonecarboxylic Acid.

In preparing phenyldehydrohexonecarboxylic acid the following method has been found to give the best results:—

Ethyl benzoylacetate (50 grams) is gradually added in small portions at a time to a solution of sodium (6 grams) in absolute alcohol (72 grams), the mixture being well cooled after each addition of the ethereal salt; the trimethylene bromide (52·5 grams) is then added, and the solution heated on the water-bath for about an hour in a flask provided with a reflux condenser. The flask is then cooled under the tap, an alcoholic solution of sodium (6 grams) added in small quantities at a time to the well-cooled solution, and the mixture heated again on the water-bath for about two hours. After distilling off the alcohol, the residue is treated with water, the oil extracted with ether, and the ethereal solution dried and evaporated.

Ethyl phenyldehydrohexonecarboxylate (58 grams) is thus obtained as a thick, brown oil, which, on cooling, partially solidifies; after keeping for about 24 hours, the crystals are separated by filtration and washed with a little alcohol. The yield of the pure crystalline compound is, on the average, 17·5 grams from 50 grams of ethyl benzoylacetate; the mother liquors still contain a large quantity of ethyl phenyldehydrohexonecarboxylate, which cannot easily be isolated, but from which it is not difficult to obtain a considerable quantity of the pure acid in the manner described below.

Phenyldehydrohexonecarboxylic acid is easily obtained in a pure condition by boiling the crystalline ethereal salt with a concentrated solution of alcoholic potash; after distilling off the alcohol, the residue is dissolved in water, the cold solution acidified with dilute sulphuric acid, the precipitated acid separated by filtration, washed with cold water, and recrystallised from alcohol. The yield is almost theoretical, 17·5 grams of the crystalline ethereal salt giving 15·3 grams of the pure acid.

A further quantity of the acid can be obtained by hydrolysing the oily mother liquors from the crystalline ethyl phenyldehydrohexonecarboxylate, as described above; after boiling for about six hours, the alcohol is distilled off, the residue treated with water, and the solution extracted twice with ether to remove acetophenone and other oily impurities. The alkaline solution is then acidified with dilute sulphuric acid, and the precipitated oil extracted with ether. On evaporating the dried ethereal solution, there remains a dark-brown oil, which soon solidifies. This product is a mixture of benzoic acid and phenyldehydrohexonecarboxylic acid; it is first spread on a porous plate to free it from small quantities of oily impurities, and then fractionally recrystallised from alcohol. In this way about 6 grams of pure phenyldehydrohexonecarboxylic acid can be obtained from the oily mother liquors produced from 50 grams of ethyl benzoylacetate, so that the total yield of the pure acid is about 23·5 grams from 50 grams of ethyl benzoylacetate.

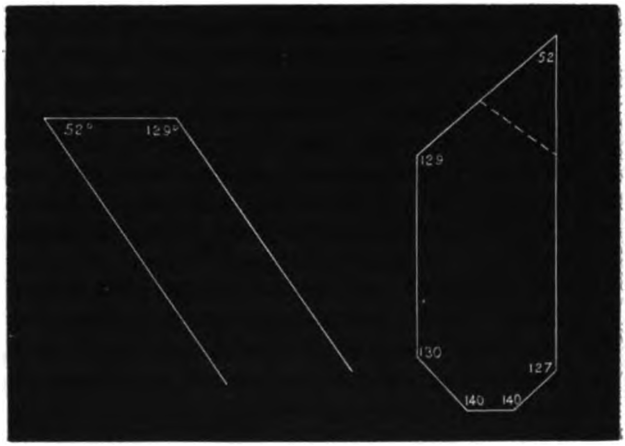
Benzoylbutyl Alcohol, $COPh\cdot[CH_2]_3\cdot CH_2\cdot OH$.

The benzoylbutyl alcohol employed in these experiments was prepared as previously described (Trans., 1887, **51**, 733), namely, by boiling finely-divided phenyldehydrohexonecarboxylic acid with a large volume of water. As soon as the evolution of carbonic anhydride is at an end, the hot solution is filtered in order to separate the phenyldehydrohexone, which is produced in considerable quantities, especially if only comparatively small quantities of water are employed. When the aqueous solution is allowed to cool slowly, some of the ketone alcohol separates in an oily condition, but when kept for a long time in the cold, the oil gradually solidifies and a considerable quantity of beautiful, iridescent crystals are obtained. As benzoylbutyl alcohol had not, up to this time, been obtained in a crystalline condition, the crystals were separated by filtration, dried for about three days on a porous plate, and then analysed with the following result—

0·2252 gram of substance gave 0·6110 gram of CO_2 and 0·1597 gram of H_2O.

	Calculated for $C_{11}H_{14}O_2$.	Found.
C........	74·15 per cent.	73·99 per cent.
H........	7·87 ,,	7·87 ,,
O........	17·98 ,,	18·14 ,,

Benzoylbutyl alcohol crystallises from water in beautiful, iridescent, transparent plates melting at 40—41°. Some of the crystals were measured under a microscope provided with a graduated circle; the measurements are given in the following diagram.



It is readily soluble in alcohol, methyl alcohol, ether, benzene, and most of the ordinary organic solvents, but only very sparingly in light petroleum.

When the crystalline benzoylbutyl alcohol is placed in a desiccator over sulphuric acid, it rapidly liquefies and is completely converted into phenyldehydrohexone according to the equation—

$$COPh{\cdot}[CH_2]_3{\cdot}CH_2{\cdot}OH = CH_2{<}\begin{matrix}CH{:}CPh\\ CH_2{\cdot}CH_2\end{matrix}{>}O + H_2O.$$

Benzoylbutyl Alcohol Oxime, $OH{\cdot}N{:}CPh{\cdot}[CH_2]_3{\cdot}CH_2{\cdot}OH$.

Benzoylbutyl alcohol oxime is prepared by treating the crystalline ketone alcohol (1 gram) with hydroxylamine hydrochloride (0·5 gram) and potash (3 grams) in cold dilute alcoholic solution. After keeping for about 24 hours at the ordinary temperature, the alcohol is evaporated on the water-bath, the residue treated with water, the solution slightly acidified with dilute sulphuric acid, and the precipitated oil extracted with ether. The thick, yellowish oil (1 gram) which remains when the ether is evaporated was kept over sulphuric acid under reduced pressure for about two days, and then analysed with the following result—

0·2109 gram of substance gave 12·4 c.c. of nitrogen measured at 20° and 752 mm.

	Calculated for $C_{11}H_{15}NO_2$.	Found.
N	7·25 per cent.	7·31 per cent.

After keeping the oil for some weeks in a desiccator, it showed signs of crystallising, and on rubbing it with a glass rod the whole solidified to a colourless, crystalline mass. The crystals were spread on a plate to free them from traces of oil, then dissolved in warm benzene, and the solution allowed to cool slowly.

Benzoylbutyl alcohol oxime is thus obtained in transparent microscopic plates melting at 56—57°. It is very readily soluble in chloroform, methyl alcohol, warm benzene, and most organic solvents, but only sparingly in light petroleum and in water; it dissolves freely in potash, in hydrochloric acid, and in concentrated sulphuric acid with development of heat, yielding a colourless solution. It is acted on by acetic chloride with development of heat; when the excess of acetic chloride is evaporated and the residual oil warmed, it assumes first a beautiful blue and then a red colour.

ω-Phenylpentamethylene Glycol, $OH{\cdot}CHPh{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$.

Phenylpentamethylene glycol is easily obtained by reducing benzoylbutyl alcohol with sodium amalgam in aqueous solution: the yield is quantitative.

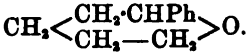
In preparing the glycol it is unnecessary to isolate the benzoylbutyl alcohol; the solution of the ketone alcohol obtained by boiling phenyldehydrohexonecarboxylic acid with water is filtered from the phenyldehydrohexone, allowed to cool, placed in a large, flat-bottomed dish, and treated with a large excess of 3 per cent. sodium amalgam in small quantities at a time. If the solution is not too concentrated, it remains almost perfectly clear during the whole operation, but if a saturated solution of the ketone alcohol is employed, it soon becomes turbid, owing to the separation of oily drops. In such cases it is necessary to add a little pure methyl alcohol in order to redissolve the oil, otherwise the reduction of the ketone alcohol may be incomplete. A purer product is, however, obtained when the solution employed is so dilute that the addition of methyl alcohol becomes unnecessary, as in this case the oily bye-products which seem to be always formed in very small quantities can be subsequently separated by filtration. The slightly turbid aqueous solution is decanted from the mercury, saturated with carbonic anhydride, allowed to cool completely, and then filtered from the crystals of sodium hydrogen carbonate. The glycol in the clear solution is extracted by repeatedly shaking with pure ether, and the ethereal extract, after drying over potassium carbonate, is evaporated.

Phenylpentamethylene glycol is thus obtained in the form of a thick, colourless oil; when kept for some time over sulphuric acid under reduced pressure, it begins to crystallise, and on stirring the oil with a glass rod, it quickly solidifies to a hard, colourless, crystalline mass, a considerable development of heat taking place. The analysis of the crystalline compound gave the following result—

0·1935 gram of substance gave 0·5199 gram of CO_2 and 0·1614 gram of H_2O.

	Calculated for $C_{11}H_{16}O_2$.	Found.
C	73·33 per cent.	73·26 per cent.
H	8·89 ,,	9·26 ,,
O	17·78 ,,	17·48 ,,

Phenylpentamethylene glycol dissolves freely in hot benzene, and on cooling quickly it separates from the solution in an oily condition; if, however, a cold benzene solution is allowed to evaporate slowly at the ordinary temperature, the glycol separates in transparent, concentrically-grouped needles melting at about 54°. It is very readily soluble in cold ether, alcohol, and ethyl acetate, but only sparingly in hot light petroleum. It dissolves moderately easily in both hot and cold water, but on adding potassium carbonate to the solution, it is partially reprecipitated as an oil or in a crystalline condition. When heated in small quantities in a test tube under the ordinary pressure, it distils without leaving any residue, and water condenses on the cooler portions of the test tube; it is probable that on distillation the glycol is converted into an oxide of the constitution



$CH_2<\begin{matrix}CH_2\cdot CHPh\\ CH_2—CH_2\end{matrix}>O$.

Phenylpentamethylene glycol dissolves in concentrated hydrobromic acid, with development of heat, and is thereby partially converted into the bromide, which separates from the solution almost immediately in the form of a yellowish oil.

ω-Phenylpentamethylene Bromide, $C_6H_5\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br$.

The only method by which phenylpentamethylene bromide can be easily prepared from the corresponding glycol seems to be to treat the glycol with phosphoric bromide in chloroform solution.

When the glycol is treated with concentrated hydrobromic acid, either in the cold or at a moderately high temperature, the product still contains a considerable quantity of the monobromide or unchanged glycol. In the first attempts to prepare the dibromide, the pure crystalline glycol was dissolved in twelve times its weight of the acid (saturated at 0°), the mixture shaken well and then heated on the water-bath for about two hours, with frequent shaking. The supernatant, dark-brown oil was then separated, dissolved in ether, the ethereal solution washed with a little dilute sodium carbonate, dried over calcium chloride, and evaporated. A bromine determination, made with a portion of this product which had been kept for 24 hours over sulphuric acid, gave the following result—

0·3018 gram of substance gave 0·2791 gram of silver bromide.

	Calculated for $C_{11}H_{14}Br_2$.	Found.
Br	52·27 per cent.	39·3 per cent.

As the analysis showed that the conversion into the dibromide was far from being complete, the crude product was again treated with hydrobromic acid exactly as described above, and the dark-brown oil analysed; the percentage of bromine had only increased to 44·6. As the failure of these experiments seemed to be due to the insolubility of the partially brominated oil in the acid, the next attempts to prepare the dibromide were carried out as follows:—The glycol, or the partially brominated compound, was dissolved in a large quantity of glacial acetic acid, the solution saturated with hydrogen bromide at 0°, and kept for three hours at the ordinary temperature. It was then largely diluted with water, the precipitated oil extracted with ether, and isolated in the usual way. This treatment gave no better results. In the last experiments which were made with hydrobromic acid, the following method was employed:—The crude bromide from a previous operation (containing 43·4 per cent. of bromine) was dissolved in about 20 volumes of glacial acetic acid, the solution saturated with hydrogen bromide at 0° and then heated at 110—120° for about eight hours in sealed tubes; the resulting dark-brown oil contained a slightly larger percentage of bromine, as is shown by the following analysis—

0·2032 gram of substance gave 0·2248 gram of silver bromide.

	Calculated for $C_{11}H_{14}Br_2$.	Found.
Br.........	52·27 per cent.	47·2 per cent.

This method not being considered satisfactory, and a purer product being required for subsequent experiments, the action of phosphorus tribromide on the glycol was investigated. The pure glycol was boiled for about an hour, in a flask provided with a reflux apparatus, with a considerable excess of phosphorus tribromide; the product obtained in this way contained about 44 per cent. of bromine, but considerable quantities of resinous substances are formed in the reaction; for this reason the yield is very unsatisfactory and the dibromide obtained is very impure.

The method of preparation finally adopted, and which gives an almost pure product in theoretical quantity, is the following:—The pure glycol is dissolved in about 30 times its weight of pure chloroform and a small quantity of phosphorus pentabromide added to the solution; a slight development of heat occurs and a copious evolution of hydrogen bromide commences at once. As soon as the action has ceased, the addition of the phosphorus pentabromide is continued, small portions being added from time to time until the amount employed is about twice the calculated quantity. After keeping the mixture for two days in a desiccator, the chloroform solution is decanted and the residual pentabromide washed with a little dry chloroform; the chloroform solutions are mixed together, washed with water, then with a little dilute sodium carbonate, and finally with water again, dried over calcium chloride, and the chloroform evaporated on the water-bath.

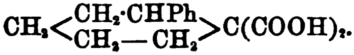
The dibromide is thus obtained in an almost pure condition in the form of a thick, almost colourless oil; bromine determinations were made with three different samples which had been kept for some time over paraffin under reduced pressure. The following are the results:—

I. 0·3416 gram of substance gave 0·4205 gram of silver bromide.
II. 0·1442 gram of substance gave 0·1750 gram of silver bromide.
III. 0·2338 gram of substance gave 0·2806 gram of silver bromide.

	Calculated for $C_{11}H_{14}Br_2$.	Found. I.	II.	III.
Br......	52·27 p. c.	50·3	51·7	51·2 p. c.

Phenylpentamethylene bromide is a thick, almost colourless oil with a pleasant, rather sweet smell; it is readily soluble in ether but only very sparingly in alcohol, and seemingly insoluble in water and in concentrated hydrobromic acid. When distilled over lime, it yields small quantities of a colourless compound which has a strong odour of naphthalene and crystallises in colourless plates; the nature of this substance has not been determined owing to the small quantity at our disposal.

Phenylhexamethylenedicarboxylic acid,



$$CH_2<\begin{matrix}CH_2\cdot CHPh\\ CH_2-CH_2\end{matrix}>C(COOH)_2.$$

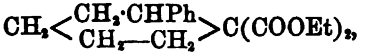
Ethyl phenylhexamethylenedicarboxylate is formed when ethyl malonate (2 mols.) is treated with phenylhexamethylene dibromide (1 mol.) and sodium ethoxide (2 mols.) in alcoholic ethereal solution; the reaction is represented by the equation—

$$C_6H_5\cdot CHBr\cdot[CH_2]_3\cdot CH_2Br + 2CHNa(COOEt)_2 = C_{14}H_{16}O_4 + CH_2(COOEt)_2 + 2NaBr.$$

This ethereal salt, on hydrolysis, yields phenylhexamethylenedicarboxylic acid.

Ethyl malonate (10·4 grams) is added in small portions at a time to a solution of sodium (1·5 grams) in about twelve times its weight of absolute alcohol, care being taken to prevent the temperature from rising above 35—40°. An ethereal solution of the dibromide (10 grams) is then added, and the mixture is heated on the water-bath in a flask provided with a reflux condenser; the addition of ether is necessary owing to the insolubility of the dibromide in alcohol. Just as the solution begins to boil, the separation of sodium bromide commences, and, after heating for about 1½ hours, the reaction is at an end. The alcohol is then distilled off, the residue treated with water to dissolve the sodium bromide, the oil extracted with ether, and the dried ethereal solution evaporated.

Ethyl phenylhexamethylenedicarboxylate,

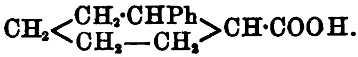


$$CH_2<\begin{matrix}CH_2\cdot CHPh\\ CH_2-CH_2\end{matrix}>C(COOEt)_2,$$

is thus obtained in the form of a thick, yellowish-brown oil, which shows no signs of crystallisation even when kept for a long time over sulphuric acid under reduced pressure. This compound was not analysed and no attempts were made to obtain it in a pure condition; its method of formation and its decomposition into phenylhexamethylenedicarboxylic acid prove that it has the constitution given above.

Phenylhexamethylenedicarboxylic acid is produced when the ethereal salt just described is boiled for 4 to 5 hours with a concentrated alcoholic solution of potash. After distilling off the alcohol, the residue is treated with water, the aqueous solution evaporated in a basin in order to expel the remainder of the alcohol, then diluted with water and filtered to free it from oily impurities. The filtrate is acidified with excess of dilute sulphuric acid, and the precipitated oil extracted with ether; on evaporating the dried ethereal solution, phenylhexamethylenedicarboxylic acid remains as a thick, yellow oil. No analysis of this compound was made owing to the difficulty of obtaining it in a pure condition; the fact that on heating it is converted into phenylhexamethylenecarboxylic acid, with evolution of carbonic anhydride, is sufficient proof that it has the formula assigned to it above.

Phenylhexamethylenecarboxylic acid,



$$CH_2{<}\begin{matrix}CH_2\cdot CHPh\\ CH_2-CH_2\end{matrix}{>}CH\cdot COOH.$$

Phenylhexamethylenecarboxylic acid can be obtained in two ways, as has been stated above; either by heating phenylhexamethylenedicarboxylic acid, or by the hydrolysis of ethyl phenylacetylhexamethylenecarboxylate.

The preparation of this compound from phenylhexamethylenedicarboxylic acid is carried out as follows:—The crude acid is placed in a small flat-bottomed flask and heated in a metal-bath at 150—160°, until the evolution of carbonic anhydride ceases; the temperature is then raised to 175—180°, and the heating continued for about 5 minutes in order to ensure complete decomposition. The residual dark-brown oil is transferred to a larger flask, and boiled for about an hour with excess of baryta; the monocarboxylic acid dissolves in the baryta, but a considerable quantity of dark-brown resinous products remain undissolved, and can be easily separated by filtration. The solution is then heated again to boiling, the excess of baryta precipitated with carbonic anhydride, the filtrate allowed to cool and treated with excess of dilute hydrochloric acid. The acid, which is precipitated as an oil, is extracted by repeatedly shaking with pure ether, and the ethereal solution dried over calcium chloride and evaporated.

The yellowish oil obtained in this way was kept over sulphuric acid under reduced pressure until its weight became constant, and then analysed with the following results:—

0·2983 gram of substance gave 0·7982 gram of CO_2 and 0·2120 gram of H_2O.

	Calculated for $C_{12}H_{16}O_2$.	Found.
C	76·47 per cent.	72·95 per cent.
H	7·84 ,,	7·93 ,,
O	15·69 ,,	19·12 ,,

The analysis having shown that the acid, purified in this way, still contains a considerable quantity of foreign substances, the oil was treated again with baryta exactly as described above, and then analysed.

0·2099 gram of substance gave 0·5644 gram of CO_2 and 0·1511 gram of H_2O.

	Calculated for $C_{13}H_{16}O_2$.	Found.
C........	76·47 per cent.	73·76 per cent.
H........	7·84 ,,	7·98 ,,
O........	15·69 ,,	18·26 ,,

The analysis showed clearly that purification with baryta is of little use after the first treatment, so that other means had to be adopted to obtain the acid in a pure condition.

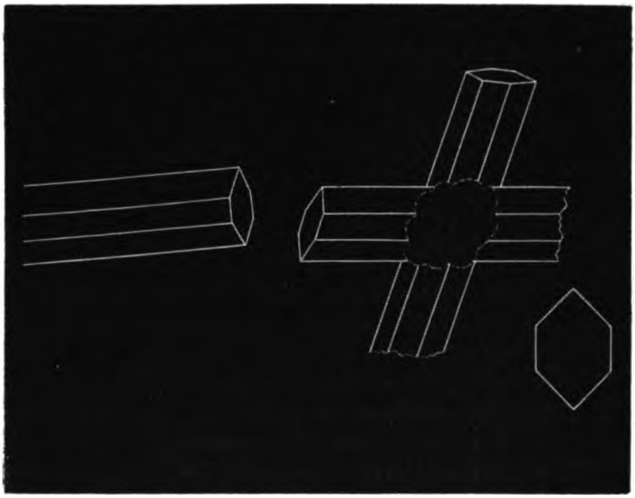
The method which invariably led to the best results was the following:—The yellow oil, obtained after treating once with baryta as described above, is mixed with a slight excess of very concentrated ammonia, and the mixture stirred well until the acid has completely dissolved; the solution is then transferred to a basin and kept in a desiccator over potassium carbonate, until the whole solidifies. The yellowish, waxy mass is spread on a porous plate and kept over potassium carbonate for a few days. The ammonium salt is thus obtained perfectly colourless and free from all oily impurities. It is dissolved in water, the solution acidified with excess of dilute sulphuric acid, and the oil extracted with pure ether. On evaporating the dried ethereal solution, there remains a thick, colourless oil, which after some time completely solidifies to a colourless crystalline mass.

The analysis of the crystalline compound gave the following result:—

0·1637 gram of substance gave 0·4536 gram of CO_2, and 0·1201 gram of water.

	Calculated for $C_{13}H_{16}O_2$.	Found.
C........	76·47 per cent.	75·57 per cent.
H........	7·84 ,,	8·15 ,,
O........	15·69 ,,	16·38 ,,

Phenylhexamethylenecarboxylic acid separates from warm light petroleum in beautiful, compact, rosette-shaped crystals; when crystallisation takes place slowly at the ordinary temperature, it separates from the solution in large, transparent, well-defined prisms. Some of the crystals were drawn with the aid of the microscope and are shown in the diagram given below.



It melts at 104—105° and is readily soluble in cold ether, chloroform, methyl alcohol, acetone, and warm light petroleum, but only moderately in the cold solvent, and insoluble or very sparingly soluble in water. When heated in small quantities under the ordinary pressure, it distils with scarcely any decomposition and the distillate solidifies again on cooling; when the acid is heated quickly to a moderately high temperature, it gives off a pungent and irritating odour very like that of acraldehyde. It is only very slowly acted on by concentrated nitric acid; it is not oxidised by potassium permanganate in cold alkaline solution, but, on boiling, the pink colour of the solution gradually disappears.

The *silver* salt, $C_{13}H_{15}O_2Ag$, was prepared by precipitating a neutral aqueous solution of the ammonium salt with silver nitrate; the precipitate was washed with cold water, spread on a porous plate, and then dried for a short time at 100°.

A silver determination with the salt thus prepared gave the following result:—

0·2796 gram of the silver salt gave 0·0983 gram of silver.

	Calculated for $C_{13}H_{15}O_2Ag$.	Found.
Ag	34·66 per cent.	35·15 per cent.

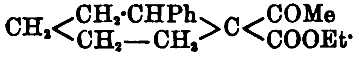
Silver phenylhexamethylenecarboxylate is a colourless, seemingly amorphous powder, only sparingly soluble in boiling water; on cooling the solution, the salt is deposited in waxy flakes. It seems to be fairly stable when exposed to light, and it is only after some hours that it acquires a slight pink tint in diffused sunlight. It can be heated at 100° for a short time without any appreciable decomposition taking place, but when heated more strongly it acquires a brilliant, green colour, and gives off vapours having an extremely disagreeable and pungent odour recalling that of burnt fat.

The *ammonium* salt can be obtained in the form of a colourless powder by dissolving the acid in concentrated ammonia and evaporating the solution at the ordinary temperature in an atmosphere of ammonia; it is very readily soluble in water.

In aqueous solutions of the ammonium salt, lead acetate, zinc sulphate, and mercurous nitrate produce colourless, amorphous precipitates, which are sparingly soluble in boiling water, and become soft and wax-like on heating. Ferric chloride produces a yellowish-brown precipitate which turns reddish-brown on warming, and is insoluble or only very sparingly soluble in boiling water. Copper sulphate gives a light-blue precipitate readily soluble in ammonia, and stannous chloride gives a colourless precipitate readily soluble in boiling water.

The salts of the alkaline earths and the magnesium salt are readily soluble in cold water, as even in moderately concentrated solutions of the ammonium salt, barium chloride, and magnesium chloride cause no precipitation.

Ethyl Phenylacetylhexamethylenecarboxylate,



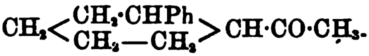
$$\mathrm{CH_2}{<}\begin{matrix}\mathrm{CH_2\cdot CHPh}\\ \mathrm{CH_2-CH_2}\end{matrix}{>}\mathrm{C}{<}\begin{matrix}\mathrm{COMe}\\ \mathrm{COOEt}\end{matrix}\cdot$$

Ethyl phenylacetylhexamethylenecarboxylate can be obtained by treating ethyl acetoacetate (1 mol.) with phenylpentamethylene bromide (1 mol.) and sodium ethoxide (2 mols.) in alcoholic solution; the reaction may be represented by the equation—

$$\mathrm{CH_3\cdot CO\cdot CH_2\cdot COOEt + C_6H_5\cdot CHBr\cdot[CH_2]_3\cdot CH_2Br + 2NaOC_2H_5 =}$$
$$\mathrm{C_6H_9Ph(CO\cdot CH_3)\cdot COOEt + 2NaBr + 2C_2H_5\cdot OH.}$$

In preparing this compound, ethyl acetoacetate (6·5 grams) is gradually added to an alcoholic solution of sodium (1·2 grams) in small portions at a time, the mixture being cooled well under the tap during the operation. The phenylpentamethylene bromide (15·3 grams) dissolved in about 10 volumes of dry ether is then added, and the mixture is heated on the water-bath in a flask provided with a reflux condenser; as the solution begins to boil, a considerable quantity of sodium bromide is deposited, and after heating for about half an hour the action is at an end. The flask is then cooled under the tap, a solution of sodium (1·2 grams) in absolute alcohol added in small portions at a time, the mixture being kept cold during the operation, and then the whole heated again on the water-bath for about two hours. The alcohol is then distilled, the residue treated with water, and the oily product extracted with ether; on evaporating the dried ethereal solution, the ethyl phenylacetylhexamethylenecarboxylate remains as a yellowish oil (14 grams). No attempts were made to obtain this compound in a pure condition, and no analysis was made; its constitution is, however, proved by its method of preparation and by its decomposition into phenylacetylhexamethylene and phenylhexamethylenecarboxylic acid as described below.

Phenylhexamethylene Methyl Ketone,



$CH_2<\begin{matrix}CH_2\cdot CHPh\\CH_2-CH_2\end{matrix}>CH\cdot CO\cdot CH_3$.

When the crude ethyl phenylacetylhexamethylenecarboxylate, obtained as described above, is hydrolysed with alcoholic potash, it is converted into phenylhexamethylene methyl ketone (phenylacetylhexamethylene) and phenylhexamethylenecarboxylic acid, according to the equations—

$$C_6H_9Ph(COMe)\cdot COOC_2H_5 + 2KOH = C_6H_9Ph\cdot COMe + K_2CO_3 + C_2H_5\cdot OH.$$

$$C_6H_9Ph(COMe)\cdot COOC_2H_5 + 2KOH = C_6H_9Ph\cdot COOK + C_2H_3O_2K + C_2H_5\cdot OH.$$

The relative quantity of the two products depends to some extent on the manner in which the hydrolysis is carried out; if the whole of the alcoholic potash is added at once, and the mixture then boiled the yield of ketone is less and that of the acid larger than when the alcoholic potash is added in small quantities at a time to the hot solution of the ethereal salt.

The following method was found to give a good yield of ketone:—The ethereal salt (13 grams) is dissolved in a small quantity of alcohol, the solution heated to boiling on the water-bath, and then a concentrated aqueous alcoholic solution of potash (24 grams) gradually added through a dropping funnel; as soon as the whole of the potash has been added, the mixture is boiled for a few minutes, and the alcohol is then distilled off. On adding water to the residue, the ketone separates as an oil, and can be easily extracted by shaking with ether; the phenylhexamethylenecarboxylic acid remains as potassium salt in the alkaline solution, and can be isolated as described below.

On evaporating the dried ethereal solution, the ketone remains in the form of a brown, moderately mobile oil, the yield of the crude product being 6·5 grams from 13 grams of the ethereal salt. When this oil is submitted to fractional distillation under a pressure of 50 mm., the thermometer rises rapidly to about 190°, and almost the whole passes over between 196° and 203°; the fraction collected between 196° and 203° was fractionated again under a pressure of 40 mm., and the portion boiling constantly at 187—190° collected separately. On cooling, this fraction solidified to a mass of colourless crystals, which were spread on a porous plate to free them from traces of oil, and then analysed.

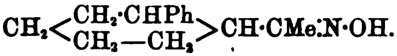
The following was the result of the analysis:—

0·1442 gram of substance gave 0·4358 gram of CO_2 and 0·1202 gram of H_2O.

	Calculated for $C_{14}H_{18}O$.	Found.
C........	83·16 per cent.	82·42 per cent.
H........	8·91 „	9·26 „
O........	7·92 „	8·32 „

Phenylhexamethylene methyl ketone is a colourless, crystalline compound, with an odour recalling that of the higher homologues of acetophenone. It melts at about 78—79°, and boils at 187—190° under a pressure of 40 mm. It is readily soluble in ether, alcohol, benzene, chloroform, and most of the ordinary organic solvents, but insoluble or only very sparingly soluble in water. It separates from cold ether in long, feathery crystals, and on adding water to a cold methyl alcoholic solution it is precipitated in colourless needles.

Phenylhexamethylene Methyl Ketone Oxime,



$$\mathrm{CH_2}<\!\begin{array}{c}\mathrm{CH_2{\cdot}CHPh}\\ \mathrm{CH_2{-}CH_2}\end{array}\!>\mathrm{CH{\cdot}CMe{:}N{\cdot}OH}.$$

The oxime was prepared by treating the pure ketone with a slight excess of hydroxylamine hydrochloride and a large excess of potash in cold, aqueous alcoholic solution. After keeping for about two days, the alcohol is evaporated on the water-bath, the residue dissolved in water, and the cold solution slightly acidified with dilute hydrochloric acid; the precipitated oil is extracted with pure ether the ethereal solution dried, filtered, and the ether evaporated.

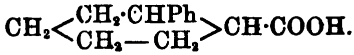
The thick, almost colourless oil obtained in this way was kept for some time over sulphuric acid under reduced pressure, but it showed no signs of crystallising. A nitrogen determination was made and gave the following result:—

0·1158 gram of substance gave 6·6 c.c. of nitrogen, measured at 16° and 715 mm. pressure.

	Calculated for $C_{14}H_{19}NO$.	Found.
N	6·45 per cent.	6·55 per cent.

Phenylhexamethylene methyl ketone oxime is a thick, almost colourless oil, very sparingly soluble or insoluble in water, but readily soluble in ether, alcohol, and most ordinary organic solvents.

Phenylhexamethylenecarboxylic acid,



$$CH_2<\begin{matrix}CH_2\cdot CHPh\\ CH_2-CH_2\end{matrix}>CH\cdot COOH.$$

The alkaline solution obtained by the hydrolysis of ethyl phenylacetylhexamethylenecarboxylate contains the potassium salt of phenylhexamethylenecarboxylic acid, as has been stated above. After extracting the ketone with ether, the solution is acidified with dilute sulphuric acid, and the precipitated oil extracted with ether; about 5 grams of the crude acid is obtained in this way from 13 grams of the ethereal salt, and an analysis of this product gave the following result:—

0·1509 gram of substance gave 0·4030 gram of CO_2 and 0·1056 gram of H_2O.

	Calculated for $C_{13}H_{16}O_2$.	Found.
C	76·47 per cent.	72·83 per cent.
H........	7·84 „	7·77 „
O.........	15·69 „	19·40 „

As the acid showed no signs of crystallisation, even when rubbed with a crystal of the substance obtained from phenylpentamethylene bromide and ethyl sodiomalonate, it was first purified by treating it with baryta as previously described. It was then dissolved in a little concentrated ammonia, the solution allowed to evaporate over potassium carbonate, and the residual ammonium salt spread on a plate to free it from small quantities of oily impurities. The salt was dissolved in dilute ammonia, the solution boiled with animal charcoal, filtered, and acidified with dilute sulphuric acid; the precipitated acid was then extracted with pure ether, and the dried ethereal solution evaporated.

The colourless oil obtained in this way soon solidified to a colourless, crystalline mass; after spreading on a porous plate and washing the crystals with a little light petroleum, they were analysed with the following result:—

0·1461 gram of substance gave 0·4078 gram of CO_2 and 1·1060 gram of H_2O.

	Calculated for $C_{13}H_{16}O_2$.	Found.
C	76·47 per cent.	76·12 per cent.
H	7·84 „	8·06 „
O	15·69 „	15·82 „

Phenylhexamethylenecarboxylic acid, prepared from ethyl acetoacetate, separates from light petroleum in crystals to all appearance identical with those of the acid obtained from ethyl malonate and phenylpentamethylene bromide. It has the same melting point (104—105°), shows a like behaviour with solvents, and gives the same precipitates with solutions of metallic salts.

Heriot Watt College,
Edinburgh.

XXIII.—*Some Crystalline Substances obtained from the Fruits of various species of* Citrus. PART I.

By WILLIAM A. TILDEN, D.Sc. Lond., F.R.S., and CHARLES R. BECK.

THE starting point of this investigation was the examination of a solid substance deposited from the écuelled essence of limes manufactured in the island of Montserrat, West Indies, for which we are indebted to the kindness of Mr. F. Watts, F.C.S., chemist to the Montserrat Company.

This substance was found to be most easily purified from the accompanying essential oil, resin, and vegetable *débris*, by dissolution in strong alcohol, and subsequent crystallisation from alcohol, to which a little caustic potash (about 1 per cent.) was added. The preparations thus obtained consisted of tufts of small prisms of a pale-yellow colour, which was not removed by repeated crystallisation from alcohol containing a larger proportion of potash.

As it will be necessary to distinguish this substance from several others derived from a similar source, we propose to call it *limettin*, the botanical name of the lime being *Citrus limetta*.

Limettin melts at 121—122°. It loses nothing when dried in the steam bath or heated to fusion. It dissolves very sparingly in water, much more freely in alcohol. It also dissolves without change in alcoholic potash or soda, and from strong solutions is immediately reprecipitated by acids; it is, however, neutral to test paper, and possesses no acid properties. It has a bitterish, styptic taste. An alkaline solution does not reduce Fehling's solution, or only to a very slight extent after long boiling. Boiled with dilute sulphuric acid, it gives no indication of the formation of a glucose, and the substance filtered from the liquid on cooling has the original melting point. Limettin gives no special coloration with ferric chloride. It contains no nitrogen.

Submitted to combustion, it gave the following percentages of carbon and hydrogen:—

	I.	II.	III.	IV.	Mean.
C	62·92	63·07	63·05	63·52	63·14
H	4·90	5·13	4·62	4·78	4·86

Three combustions made for us by Mr. A. L. Stern, B.Sc., gave the following numbers:—

	I.	II.	III.	Mean.
C	63·36	63·38	63·12	63·29
H	4·80	4·67	4·68	4·71

From these results it appears that the formula of limettin is $C_{16}H_{14}O_6$, as shown by the following comparison:—

		Experiment. T. and B.	Experiment. Stern.	Calculated. $C_{16}H_{14}O_6$.
C_{16}	192	63·14	63·29	63·57
H_{14}	14	4·86	4·71	4·63
O_6	96	32·09	32·00	31·80
	302			

A bromo-substitution compound can be obtained by dissolving the substance in alcohol, or much better in glacial acetic acid, and adding an excess of bromine dissolved in a portion of the same solvent. It crystallises in colourless scales which gave 43·56 per cent. of bromine. It therefore contains 3 atoms of bromine; $C_{16}H_{11}Br_3O_6$ corresponds to 44·52 per cent. of bromine. Limettin is not attacked by acetyl chloride when heated with it for about four hours, in a sealed tube, at the temperature of the water-bath; it therefore seems to contain no hydroxyl. When heated to about 160° with concentrated hydrochloric acid, limettin is converted into a red resinous substance, but no gaseous or volatile alkyl chloride is produced. Dissolved in strong acetic acid and digested on the water-bath with excess of phenylhydrazine for some hours, there is no perceptible reaction, and no hydrazone is produced.

When the substance is heated above its melting point, the colour deepens, and at about 200° it boils. On distillation it yields a black charred residue, and a yellow distillate which solidifies on cooling. After dissolution of the latter in alcohol, it crystallises in pale-yellow, silky needles, somewhat different in appearance from the original substance, and melting at 140°. Submitted to combustion, it gave—

	I.	II.	III.	Mean.
C	64·87	64·21	64·34	64·47
H	5·30	5·14	5·03	5·16

This substance requires further investigation.

Evidence regarding the relationships of limettin was obtained by fusing it with potash; 30 grams of limettin were boiled for about an hour in a flask with 100 grams of potash and 100 grams of water, until very concentrated. The substance dissolved very slowly, and no hydrogen or vapour was evolved. When cold, the solid brown mass was dissolved in water, and acidified with hydrochloric acid, which caused copious effervescence of carbon dioxide, and the formation of a brown precipitate of resinous matter. The filtered liquid was extracted with ether, and the watery solution submitted to distillation. The ethereal extract yielded crystals of phloroglucol; this was identified by its sweet taste, by the violet coloration with ferric chloride, by staining deal wood, by the formation of the characteristic red azobenzene-compound, and by a determination of the water of crystallisation. The air-dried crystals lost at 100° 22·2 per cent. of water; $C_6H_6O_3 2H_2O$ corresponds to 22·2 per cent. The melting point was about 210°.

Acetic acid and a small quantity of formic acid are contained in the aqueous distillate. Other fatty acids were carefully sought for, but were not detected. When caustic potash without addition of water was employed, and the fusion effected at a higher temperature, gas was evolved, and acetic acid the only isolable product.*

When limettin is boiled for some time with a strong solution of caustic potash or soda, without allowing the liquid to become concentrated by evaporation, it slowly dissolves, and on acidifying it is precipitated to all appearance unchanged. The recovered substance, however, melts at 147°, and by combustion gave—

C.....................	64·40	per cent.
H	4·60	,,

---

* We found that phloroglucol alone fused with potash yields acetic acid; probably thus: $C_6H_6O_3 + 3KHO = 3C_2H_3KO_2$.

This corresponds to $C_{14}H_{12}O_5$, which requires—

C....................	64·61 per cent.
H	4·61 „

A small quantity of acetic acid is found in the liquid. This substance is evidently the result of a process of saponification; it contains the elements of limettin in which an acetyl group has been displaced by hydrogen.

$$C_{14}H_{11}(O{\cdot}C_2H_3O)O_4 + NaHO = C_{14}H_{11}(OH)O_4 + NaO{\cdot}C_2H_3O.$$

The product of destructive distillation already described is possibly the same substance; the hydrogen found in that compound was, however, ½ per cent. higher.

Treated with nitric acid, limettin yields chiefly oxalic acid, with a small quantity of an undetermined nitro-acid.

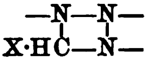
The facts related can be explained by the hypothesis that limettin is an acetic derivative of a kind of anhydride, which by hydrolysis yields phloroglucol.

This substance evidently does not agree in any of its properties with either of the substances hitherto obtained from the fruits of the different species of *Citrus*, and described under the names aurantiin, hesperidin, and limonin respectively. A brief synopsis of the sources and characters of these substances will be given at the end.

The greasy deposits which are well known to form in essence of bergamot and of lemon have been shown to contain crystalline constituents (Hanbury and Flückiger "Pharmacographia"), but these have never been closely examined. Under the impression that the crystalline constituent in the deposit from lemon oil would probably be identical with that obtained from limes, we applied to Mr. C. Umney, F.C.S., of the firm of Wright, Layman, and Umney, for a supply of the raw material, and he was good enough to collect a few ounces of the deposit from essence of lemon for us.

The greasy mass was mixed with about an equal volume of alcohol, and strained through calico. The pasty residue was then boiled with strong alcohol containing about 2 per cent. caustic soda, and filtered hot from the brown mud, consisting of fruit pulp and dirt. On cooling, the solution solidified to a jelly, which was broken up, and the liquid drained off as completely as possible. The brown alcoholic solution was then heated to boiling, acidified with hydrochloric acid, and mixed with hot water till slight turbidity was produced. On cooling, a copious crystallisation of small, flat prisms was obtained. These were purified by repeated crystallisation from strong alcohol.

The substance thus prepared forms yellow, lustrous needles. We closed rings. The first compounds experimented with were those containing an azo- and a benzylidene-group in the ortho-position, as it seemed probable that the groups —N:N— and X·CH:N— would condense under these circumstances with the formation of a triazine ring—

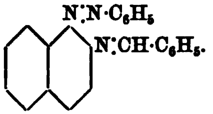


$$\begin{array}{rl} & —\mathrm{N}—\mathrm{N}— \\ & \quad\;| \quad\;\; | \\ \mathrm{X{\cdot}H}\!\!\!\! & \mathrm{C}—\mathrm{N}— \end{array}$$

Goldschmidt and Rosell have arrived at this result in the case of orthamidoazotoluene and benzeneazo-β-naphthylamine by heating these compounds with benzaldehyde. I had performed similar experiments with the same results some time before the appearance of the paper referred to, and need only state now that I can confirm the statements of the authors in so far as this method is concerned.

With respect to the triazine from benzeneazo-β-naphthylamine, I have now to describe the method by which this compound was first prepared, inasmuch as this method reverses the mode of combination effected by the authors referred to, and at the same time throws much light on the constitution. The benzylidene-derivative of the base experimented with is first prepared in the usual way, namely, by heating with one molecular proportion of benzaldehyde in alcoholic solution. The azo-derivative is then formed by diazotising the aniline, &c., and adding the solution of the diazo-salt to the cold alcoholic solution of the benzylidene-derivative. In the case of toluidine, this method fails, inasmuch as diazobenzene salts could not be made to combine with benzylidene-paratoluidine under the conditions mentioned. It was for this reason that the other method of working, which has since been made known by the German investigators, was resorted to. With β-naphthylamine the method succeeded perfectly, the formation of an azo-derivative and its subsequent conversion into the triazine being completely under control, a condition which evidently does not hold good when benzeneazo-β-naphthylamine is heated with benzaldehyde in some common solvent, as, under the influence of the high temperature which has to be employed to bring about combination (140° according to Goldschmidt and Rosell), condensation to the triazine ring at once takes place.

On adding a solution of diazobenzene chloride to a cold alcoholic solution containing the calculated quantity of benzylidene-β-naphthylamine, a deep red colour is at once developed, but no separation of colouring matter takes place till the solution is diluted with water and made basic with ammonia. A bright red precipitate is then thrown out, which gradually subsides to the bottom of the beaker, and on standing cakes to a red, resinous mass. The substance thus obtained is no doubt the azo-compound—



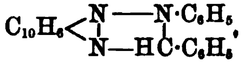
It forms a red, viscid resin, which slowly solidifies to a brittle mass of a bright-scarlet colour on standing for many days under water. The substance could not be crystallised from any solvent, as it separates from all its solutions in the form of a red varnish. Moreover, on heating the solution, gradual transformation into the triazine takes place. The substance appears also to undergo a similar change when heated to fusion in the dry state. The melting point is for this reason vague, namely, 65—90°, rising after each repetition of the determination with the same specimen. This benzylidene azo-compound is readily soluble in benzene, chloroform, ether, and acetone; somewhat less soluble in alcohol and petroleum. It possesses a distinctly basic character, dissolving in alcoholic solution of hydrogen chloride with a red colour. This property accounts for the circumstance that no precipitate is formed on mixing the solutions of the constituents.

The most interesting property of the azo-compound is the readiness with which it undergoes intramolecular transformation into the triazine. The change is best effected by heating the substance for a few minutes in glacial acetic acid. The solution is at first red, but the colour rapidly disappears, and on pouring into cold water the triazine separates as a whitish powder; this is collected, washed with cold water, and purified by treatment with alcohol mixed with strong hydrochloric acid. This solvent removes a resinous impurity, and leaves the hydrochloride of the triazine. The latter salt is easily decomposed by water, and the base thus obtained, when dried, may be purified by crystallisation from toluene. The base dissolves but slowly in toluene, and its separation in the crystalline form may be promoted by diluting the solution with light petroleum. The compound is thus obtained by slow crystallisation in the form of rosettes of dense, white, flattened needles having a melting point of 193—194°. The characters of the substance have already been given by the German investigators, and need not be redescribed. Its composition was ascertained by the following determination of the nitrogen:—

0·1560 gram gave 16 c.c. moist N at 10° C. and 755·5 mm. bar.

	Calculated for $C_{23}H_{17}N_3$.	Found.
N	12·54 p. c.	12·19 p. c.

According to its mode of formation from the benzylidene azo-compound, the formula of the triazine may be written—



$$C_{10}H_6<\begin{array}{l}N —— N\cdot C_6H_5\\ N — HC\cdot C_6H_5\end{array}.$$

The compound may be described as diphenyl-$\alpha\beta$-naphthotriazine. It is proposed to continue the investigation of this and other triazine-derivatives prepared by the method of condensation described in the present communication.

Finsbury Technical College.

XXV.—*The Nature of Solutions, as Elucidated by the Freezing Points of Sulphuric Acid Solutions.*

By SPENCER UMFREVILLE PICKERING, M.A.

THE present communication is an account of determinations of the freezing points of solutions of sulphuric acid, made with a view to obtain still further evidence of the existence of hydrates in solution than had been obtained by a study of their densities, heat of dissolution, &c. (Trans., 1890, **57**, 64).

The Determinations, and the Methods Employed.

The determinations may be divided into three classes:—(1.) Those made with very weak solutions, of which the freezing point was not lower than −1·7°. (2.) Those made with stronger solutions, of which the freezing point was not lower than −20°. (3.) Those made with very strong solutions, of which the freezing point was, in extreme cases, as low as −75°.

A. *Weak Solutions.*

The method used for these was the same as that adopted by Raoult, and most other workers on the subject. It may be conveniently distinguished as the "crystallisation" method.

About 100 c.c. of the solution were put into a wide test-tube, fitted with a perforated stopper, through which passed, (1) the stem of a delicate thermometer (reading to 0·0005° C., 0·05 mm., by estimation); (2) the rod of a stirrer made out of a circular piece of platinum foil;

and (3) a small short glass tube, through which a piece of platinum wire with a slight deposit of hoar-frost on it could be passed, in order to start the crystallisation of the water when required.

The tube was immersed in a freezing mixture of ice and hydrochloric acid, the latter having previously been diluted with about an equal volume of ice-cold water. The temperature of such a mixture is about −10°. As soon as the temperature of the solution had fallen to 0·7° below its freezing point, it was "touched off" with the platinum wire. The temperature rises rapidly, and, if the solution is very weak, remains (apparently) stationary for some seconds, after which it falls; in the case of solutions of a strength of about 1·0 per cent., the temperature begins falling the instant after it has attained the maximum, and, the stronger the solution, the more rapid is the fall. This fall is due to the fact that the tube is kept immersed in the freezing mixture all the time, and, as more ice becomes crystallised out of the solution, the latter becomes stronger, and its freezing point lower. In fact, this method must always give the freezing point of a solution stronger than that which is taken; and considerably stronger, too, for, unless there be a moderate quantity of ice formed in the liquid, the latter will be partially superfused, and its temperature will be abnormally low. The thermometer, in fact, takes the temperature of the *liquid*, and this temperature is conditioned by the surrounding freezing mixture, which tends to lower it, and the solidification of the water, which tends to keep it constant; the more solid water there is present, the less will the liquid be superfused. This explains the apparent anomaly which was always noticed, of the temperature not rising to as high a maximum as it should, if the liquid had not been cooled low enough (0·5° below its proper freezing point) before being "touched off."

The degree to which the solution is superfused, as well as the temperature of the freezing mixture, will affect the amount of ice crystallised out and the temperature registered. To guard against an error from the latter source, a fresh freezing mixture was made for every other determination, it being used first in the second determination with every solution. If the two determinations differed by more than 0·001° or 0·002° (according to the strength of the solution under examination), further determinations were made.

This method yields results of very doubtful accuracy with solutions containing more than 5 per cent. of sulphuric acid, and is quite inapplicable to 10 or 20 per cent. solutions. Not only is the strength of a strong solution affected much more than that of a weak one by the separation of a given quantity of ice from it, but the separation takes place very slowly. The crystallisation of *ice* from a solution is, in fact, precisely analogous to the crystallisation of a *salt* from a solution, and the stronger and more viscous this is, the more slowly does the solid separate or redissolve.

I tried various modifications of the procedure, but found that the one just described gave the best results. On allowing the liquid to crystallise without superfusion, or on removing the freezing mixture as soon as crystallisation had begun, very unsatisfactory results were obtained.

The main object in the present work was to obtain concordant results throughout the series, but the correct determination of the absolute values was of course desirable. I think that I have succeeded in estimating the actual error in these determinations in the following way. The lowering of the freezing point of water is, up to about 9 per cent. in the present case, roughly proportional to the strength of the solution, either percentage, or that expressed by the number of foreign molecules to 100 H_2O, a form of plotting, be it noted, very different from that according to molecular composition expressed in terms of the number of water molecules present to each H_2SO_4. The heat capacity of these solutions does not differ much from unity, and consequently the heat absorbed in cooling any of them to the same distance below its freezing point will result in the crystallisation of the same amount of water in all cases, and the strength of the solution will thereby be increased by an amount directly proportional (roughly speaking) to the strength of the solution taken; the error of the freezing point will, as a consequence, be also proportional to the strength, and to the temperature at the freezing point.

Three solutions of different strengths were taken; each of them was cooled down very slowly to different distances below its freezing point, touched off, and then placed in a bath at the same temperature as itself, the contents of the bath consisting of some of the same solution partially frozen. The temperature to which the thermometer rises in such a case is dependent on the degree to which the solution was supercooled before being touched off, and, in accordance with the above deductions, was found to be directly proportional to it. With the four or five points obtained in each case for different touching off temperatures (the lowest being but 1·6° below the freezing point), we can draw a straight line, which will give the freezing point which would have been observed had the liquid been touched off *at* the freezing point itself, that is, when the amount of crystallisation would have been infinitely small, and the composition of the liquid would have been unaltered thereby.

The three solutions gave the following results:—

Strength.	True f. p. found as above.	F. p. when touched off 0·7° below f. p.	Correction for each 1° of obsrvd. f. p.
1·1 p. c.	−0·4405	−0·4647°	0·053°
1·5 „	−0·5864	−0·6219°	0·057°
2·24 „	−0·8866	−0·9334°	0·050°
		Mean	0·0535°

The corrections for every 1 per cent. of strength are 0·023°, 0·024°, and 0·022° in the three cases respectively; mean 0·023°.

These values are very concordant, and the correction is further verified by comparing the values thus obtained with those given by the method to be described next, a method which gives, I believe, the theoretical freezing point: thus, taking the readings of diagrams representing the two sets of results, we get—

Strength.	F. p. corrected, 1st method.	F. p., 2nd method.
4·0 p. c.	−1·585	−1·61
3·5 „	−1·380	−1·38
3·0 „	−1·181	−1·16

The error is not greater than that which may be attributed to the determinations by the second method.

In spite of this concordance, however, I am very doubtful as to the value of the correction, and have, therefore, given the observed freezing points in Table I as well as the corrected ones. A fourth solution (0·75 per cent.), examined in the same way as the above, gave results which formed a curve instead of a straight line, and similar determinations which I have lately made with solutions of calcium chloride also gave curves, and, furthermore, led to very inconsistent results. For various reasons, which I need not enter into at present, the determinations offer very great practical difficulties.

Raoult (*Ann. Chim. Phys.* [6], 11, 97) found it difficult to use this crystallisation method for the freezing points of water or of very weak solutions, owing to the caking of the ice on the inside of the tube. I have found no great difficulty in doing so. It is only necessary that the freezing mixture should not be too cold—ice and the strongest hydrochloric acid is so—and that the liquid, while being cooled, should be stirred vigorously. In the present work the freezing point of water was determined at the beginning and end of each day's work. The water used was distilled with special care by Messrs. Hopkin and Williams, and was kept for the same length of time in bottles of the same glass as the solutions which had been made up with it.

To avoid false irregularities in the series of results introduced through errors in the determination with water, solutions of consecutive strength were examined on every third day.

Two series of determinations were made by this method, using a different thermometer and different solutions in each. The first series extended to a 4 per cent. solution, the second, which was the fuller and more accurate of the two, extended to 1·8 per cent. only.

Each value quoted in Table I is the mean of at least two observations. The average difference between single observations and the arithmetical mean was found to be 0·00066° in Series II, so that the mean error of these means would be about 0·0006° or 0·0005°, making allowance for the fact that the mean is sometimes deduced from two, and sometimes from three or four determinations. With the stronger solutions of Series I, it would be somewhat greater.

The concordance of the two series may be judged by the following comparison of the values deduced from the smoothed curves drawn to represent them:—

	Freezing point.		
P. c. H_2SO_4.	Series I.	Series II.	Diff.
0·05	−0·0260°	−0·0263°	+0·0003°
0·10	−0·0515	−0·0492	−0·0023
0·20	−0·0899	−0·0911	+0·0012
0·50	−0·2135	−0·2054	+0·0009
1·00	−0·4090	−0·4018	−0·0072
1·50	−0·5896	−0·5846	−0·0059

The magnitude of the error in the last two cases is probably due to the touching off temperature having been somewhat different in the two series; the values for the weaker solutions are concordant within the limits of the experimental and thermometric errors.

B. *Stronger Solutions.*

The method devised for determining the freezing points of stronger solutions consisted in ascertaining the temperature at which the last trace of solid dissolved on heating the partially frozen solution. It may be distinguished as the "dissolution" method, and, I believe, gives the true freezing, or, rather, melting point.

About 300 or 400 c.c. of the solution are placed in a glass beaker and cooled down till a good crop of crystals (ice or otherwise) is obtained. The beaker is then suspended through a hole in the cover of a large bath holding several gallons of water. A thermometer, and a stirrer worked by an electromotor are placed in the beaker, access of air being prevented, as far as possible, by a perforated cover. The thermometer is then read at intervals of half a minute. As long as any solid remains undissolved, the temperature rises very slowly, and at a practically regular rate, but, as soon as the solid has all dissolved, the rate becomes much greater. The various readings when plotted out form a diagram, consisting of two lines, representing the two rates of heating, and the point of junction of these gives the exact temperature at which the rate changed, and hence the exact temperature at which the last trace of solid disappeared.

FIG. 1.—Results of a "Dissolution" Determination.

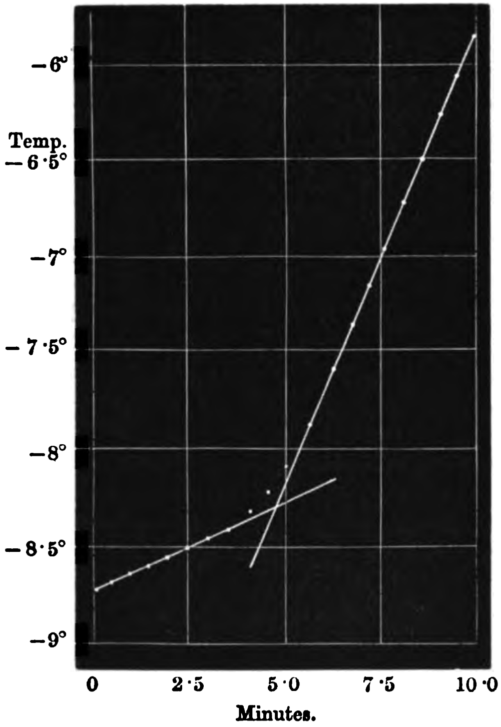


Fig. 1 gives a sketch of the readings in one determination. The two rates of increase merge gradually into one another, there being generally two to four observations, which lie on neither branch of the figure; these represent the conditions when there is still a little solid left, but not enough to keep the temperature of the liquid down as low as it should be. The rate of cooling decreases perceptibly as the temperature rises, the line BC being always curved. In dealing with a pure substance, such as H_2SO_4 or $H_2SO_4H_2O$, the line AB is horizontal, the temperature remaining constant till fusion is complete.

The rapidity of the rise may be regulated by altering the bulk, or the temperature, of the water in the bath.

The method is somewhat tedious, as many as 20 or 30 readings of the thermometer being made in each determination; but the regularity and number of these readings, when plotted out, afford a sure test of the success of the determination.

The thermometer read to 0·01° (0·1 mm.) by estimation, and, judging from the conformity of the results with the smoothed curves drawn to represent them, the average error would be 0·01° to 0·02° when water or sulphuric acid crystallised out, and 0·06° when the monohydrate did so, the last one or two determinations at exceptionally low temperatures being omitted in each case.

The lower the temperature, the less marked is the difference between the two rates of heating, and the less exact, therefore, is the determination: the difficulty of cooling a considerable bulk of liquid so as to get a good crop of crystals precludes the use of the method for solutions showing a depression of more than about 20°: it is also inapplicable for very weak aqueous solutions and for water itself, owing to the ice forming in large cakes in these cases.

The long range of temperature throughout which the observations extend in some determinations (sometimes 10° or more), and the rapidity of the rise after the solid has dissolved, render it impossible to use a delicate thermometer. The instrument used was compared with a standard thermometer at 14°, and the position of the freezing point of water on it determined: from these observations the temperatures below 0° were deduced, on the assumption that the coefficients of expansion were constant throughout.

C. *Strongest Solutions.*

With solutions causing a depression of more than 15° or 20°, only approximate results could be obtained. The liquid was cooled in a test-tube, by means of solid carbon dioxide or liquid nitrous oxide, till it crystallised, and the temperature at which the crystals just disappeared, on allowing it to rise, was determined by an alcohol thermometer. The temperatures extended to below −70°, and apparently, the error, even here, rarely exceeded 1°. At higher temperatures, where these results overlap those obtained by the dissolution method, the error would appear to be but a few tenths of a degree.

Acid Used.

The acid used was prepared for me by the kindness of Dr. Messel, and was different from any used in my previous work. Compared with this former lot which had been analysed, it gave results corresponding to 100·9524 per cent. H_2SO_4 (see Trans., 1890, **57**, 72); but, on determining its freezing point after dilution with various small proportions of water, this value appeared to be too low. The freezing points of very strong solutions, as will be seen below, constitute a figure with two branches, rising to meet at a sharply marked angle, and this maximum point *must* coincide with the pure acid. The freezing point of any crystallising substance must be, and, as a matter of experience, invariably is, lowered by the addition of a foreign body, and no mixture or impure substance can have a higher freezing point than the pure substance itself; therefore, this maximum must correspond with H_2SO_4 itself. According to these results, the stock acid contained SO_3 represented by 101·0243 per cent. H_2SO_4.

The weaker acids were prepared by the addition of ice, and subsequently of water, to weighed quantities of the strong acid.

Results obtained.—General Nature of the Action.

Tables I and II give the results obtained by the crystallisation and dissolution methods respectively. The determinations made with an alcohol thermometer are marked by an asterisk. Doubtful results are enclosed in brackets; and such duplicates as are quoted were made on different days, and with different samples of the same solutions. The percentage, as well as the molecular composition, is given, but, as the figures obtained on plotting the results according to these two methods resemble each other in every important particular, I have illustrated here but one of them, that according to percentage composition.

FIG. 2.—Freezing Points of Sulphuric Acid Solutions.

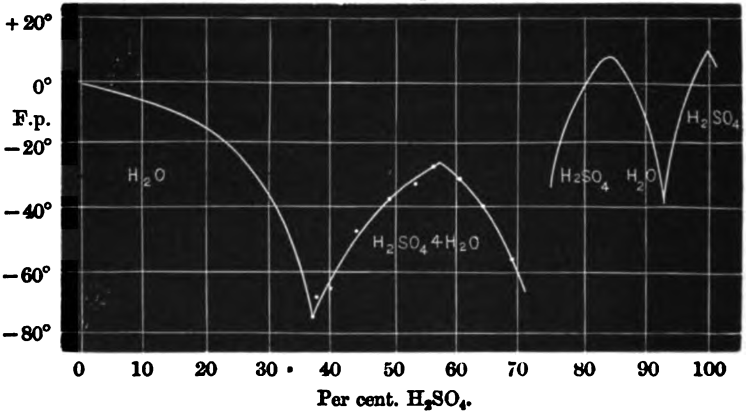


Fig. 2 shows the general nature of the diagram produced. Water crystallises from the weaker solutions, and the lowering of the freezing point increases with approximate constancy till the strength reaches 8 or 9 per cent. (nearly $2H_2SO_4100H_2O$); it then begins to fall more rapidly, being represented by a curve of increasing dip, till it reaches $-75°$ at 38 per cent.

Looking at the other end of the diagram, where the substance crystallising is H_2SO_4, it will be seen that a maximum (10·352°) of a most pronounced character is attained at the composition of the pure acid, the freezing point falling very rapidly on the addition of excess, either of SO_3, or of water, it being represented in the latter case by a line which is very nearly straight.

The crystallisation of the acid, H_2SO_4, ceases at about 76 per cent., and the crystallisation of the monohydrate begins. The freezing point rises rapidly, forming an abrupt curve, which very suddenly changes to a gentle one, and attains a maximum at 8·53°, where the composition is exactly that of the monohydrate (84·5 per cent.): it then falls again, in a manner analogous to that in which it had risen. The maximum here is rounded off in a way which affords a striking contrast to the maximum at H_2SO_4.

Isolation of the Tetrahydrate.

At the time when the preliminary notice of these results was communicated to the Society (Proc., 1889, 106), I had not succeeded in obtaining any crystallisation of solutions between 76 and 38 per cent. The nature of the water and monohydrate curves rendered it extremely improbable, however, that these would ever meet, and it seemed equally improbable that intermediate solutions would never freeze at all; I concluded, therefore, that a fresh curve, representing the crystallisation of some unknown hydrate, would fill the unoccupied space, and that that hydrate must be either $H_2SO_45\frac{1}{2}H_2O$ or $H_2SO_44H_2O$; for the monohydrate curve had already reached nearly as far as the composition of $H_2SO_42H_2O$ (73·3 per cent.), and these three hydrates were, according to my former work, the only ones which existed between the percentages of 76 and 38.

On cooling solutions of various strengths, I obtained a crystallisation, and a series of freezing points which formed two curves meeting at a well-defined angle at 57·6 per cent., and, as the composition of $H_2SO_44H_2O$ is 57·66 per cent., this concordance left no doubt that the substance crystallising was this hydrate.

This new compound forms hard, and generally large, well-defined crystals: they resemble the monohydrate in their general appearance, and re-dissolve in the liquid but slowly. The melting point of the pure tetrahydrate is −25°; but, just like the monohydrate and sulphuric acid itself, the liquid may often be superfused 20° or 30° below its freezing point.

It may still be an open question in the opinion of some people whether the crystallisation of a substance from a liquid proves its existence in that liquid, but the isolation of this hydrate would in any case afford considerable weight to my previous conclusions that it existed in solution; for, I recognised it *first* in solution, and *subsequently* proved, by isolating it, that it did exist: nor were the probabilities in favour of my having first mentioned this hydrate by mere chance, for, between the hydrates with 2 and $9H_2O$ (73 and 38 per cent.) there are 11 possible hydrates (H_2SO_4 combining with half molecules of water); of these I named but two as existing, and the one isolated is one of these two.

But the mere fact that a solid crystallises out must prove, I think, that the liquid contained some of that substance in solution. The mechanism of the action offers four different possibilities:—(1.) That the constituents of the hydrate, water and sulphuric acid, solidify separately in the proper proportions, and subsequently combine: this view is obviously untenable, and may be dismissed at once; (2) that the molecular aggregates, $x(H_2SO_44H_2O)$, of which the solid is composed, are formed directly from the H_2SO_4 and H_2O molecules: this means that no fundamental molecule of the hydrate exists, and leaves us with the impossibility of explaining how these solid aggregates can hunt each other out, and congregate to form large crystals; (3) that the fundamental molecules of the hydrate are formed in solution, but cannot remain there, and, consequently, separate almost immediately: this is tantamount to saying that the hydrate is an insoluble substance, a proposition which is most improbable in the case of a compound of sulphuric acid and water, and directly opposed to the fact that it forms well-defined large crystals; for, an insoluble substance is always, I think, deposited in the amorphous condition: indeed the formation of a crystal implies that the molecules, before they are solidified, are capable of movement towards any already solidified molecules, the process of solidification in such a case being a gradual one, and the more gradual it is, the larger are the crystals formed; (4) that the molecules of the hydrate are formed in the liquid, and exist there till the temperature is lowered to its freezing point. This, I think, is the only tenable supposition.

Indeed, when a liquid freezes and melts at a definite temperature, when the temperature remains constant till the whole of the liquid is frozen,* when any alteration in its composition lowers its freezing point, we have the most certain evidence yet adduced for regarding that liquid to be a definite, though possibly somewhat dissociated compound. If we deny this argument when applied to the hydrate in question, we must deny it in all cases, and conclude that neither the monohydrate, nor sulphuric acid itself, nor, indeed, any other liquid, is a definite substance. The argument is precisely analogous to that depending on a constant boiling point.

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* The rough determinations made were insufficient to show whether the temperature remained quite constant throughout the freezing, but it is inevitable that

Of course it cannot be argued that the fact of the existence of a liquid hydrate at −25° implies its existence at the higher temperatures of 8° to 38°, at which my density and other determinations were made: on the contrary, I only argue that because it existed, according to these latter results, at the higher temperatures, it must exist at the lower ones, and having proved this to be the case, I hold that the premises on which this conclusion rested must be correct. It may be pointed out, however, that the existence of a liquid hydrate at low temperatures would generally imply its existence at considerably higher ones. The present work, although referring to temperatures 10° to 100° lower than my previous work, reveals but one hydrate which had not already been indicated at the higher temperature; similarly, a range of 30° in the density results was found to affect the sharpness with which most of the hydrates were indicated to only a very small extent.

The only portion in which no crystallisation has yet been obtained is between 69 and 76 per cent. I thought it probable at first that the dihydrate (73·3 per cent.) might be obtained here, but I doubt this now. The absence of any crystallisation in this region is not, I think, due to the lowness of the freezing points of the solutions, but to the pasty condition ot the liquid, which means a sluggishness of motion such as would prevent a sufficient number of liquid molecules coming together to form a solid aggregate. Some of the solutions here have been cooled down to −110° without solidifying: they can scarcely be termed liquids then; though perfectly clear, they are so viscid that the thermometer cannot be drawn out of them. The last freezing point obtained on the monohydrate curve (at 76 per cent.) is not very low, about −22°, but in order to get any crystallisation in this case, the liquid had to be touched off at −80°, and kept at that temperature for a considerable time.

I imagine that there exists either another solid hydrate of sulphuric acid, or, more probably, perhaps, a modification of the monohydrate, possessing a melting point, or degree of solubility, different from that of the ordinary one (as is the case with the tetrahydrate of calcium

it must do so, where the composition of the crystals is the same as that of the liquid which yields them; in other words, wherever the freezing point is situated at a maximum.

chloride; see Roozeboom, *Rec. Trav. Chim. des Pays-Bas*, **8**, 1, fig. I), for in the case of solutions of about 90 per cent. strength, it was found that after the ordinary monohydrate had dissolved, there was left a slight deposit of small crystals, and, in one case (90·566 per cent.), the melting point of these was determined, and found to be 5·663° above that of the ordinary monohydrate, that is, the solution on being heated up in the determination by the "dissolution" method gave two distinct melting points.

Details of the Various Curves.

The four distinct curves constituting the general results represent, it must be remembered, four distinct actions, and the meeting points of any two of these must not be regarded in the light of breaks, or changes of curvature, such as would indicate the existence of hydrates in solution. Their position may be determined entirely by the alteration in the composition, and not of the constitution, of the solution, and alterations in the latter must be looked for solely in irregularities and sudden changes of curvature exhibited by these main curves.

The different scales on which I have plotted the results are very numerous, but I think it unnecessary to give any details respecting them.

A. *The Water Curve.*

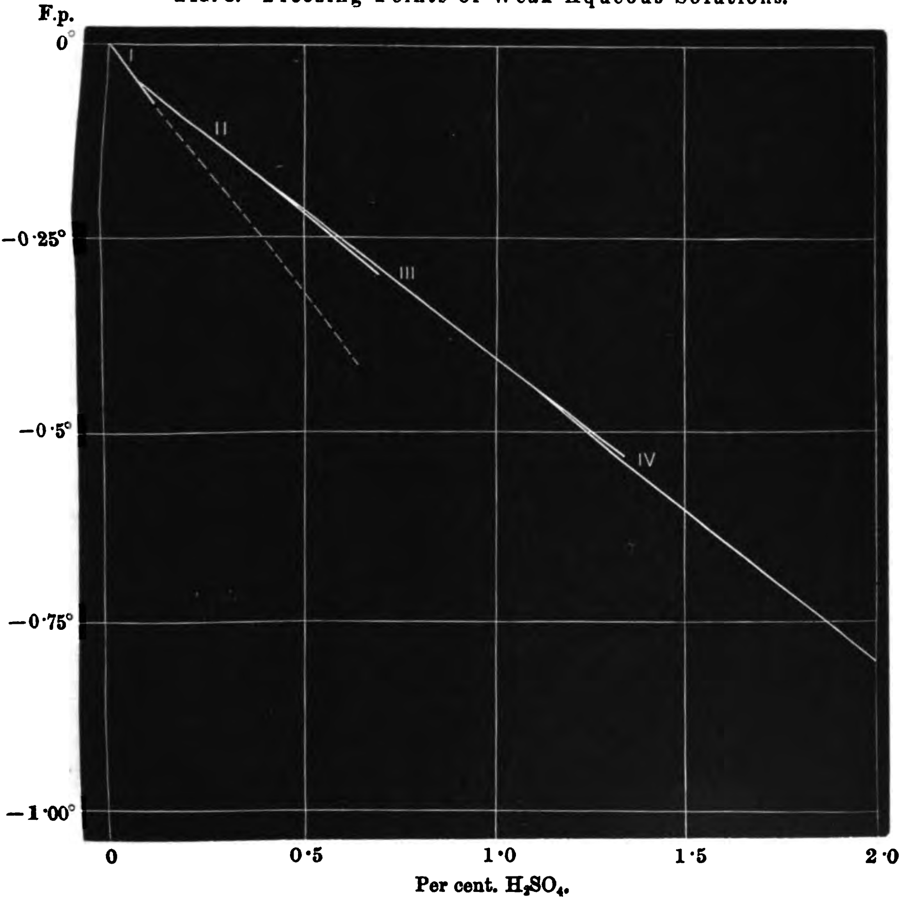
(1.) *Very Weak Solutions.*

Fig. 3 is an illustration of the results of Series II of the "crystallisation" determinations. The line marked IV may be extended to 4 per cent. by the plotting of Series I, and exhibits a very slight amount of curvature. The two series give figures which differ only in unimportant details.

The results form four independent straight, or nearly straight, lines, which cut each other on prolongation, the prolongation having been shown here in order to render the changes more distinct. The change at 1 per cent. is certainly doubtful, and its omission would make but a small increase in the error of the points. According to the first series of determinations, there may be a slight amount of curvature about the line III, and, according to this series also, the lines I and II do not appear to meet, a result, no doubt, of some error and the comparative paucity of the points determined. In the case of the more accurate series, II, there are 11, 12, and 13 experimental points on the lines I, II, and III respectively, and the average error which they exhibit as compared with the drawing is 0·0008°, there being but five cases in which it exceeds twice this amount;

this error agrees well with the mean error of 0·0006° deduced above from the observed concordance of duplicate determinations.

FIG. 3.—Freezing Points of Weak Aqueous Solutions.



These results with dilute solutions are, on the whole, very satisfactory in the evidence which they afford of sudden changes in the nature of the solution. With Series II, the points between 0 and 1 per cent. lie so evidently on different straight lines, that to depict them otherwise would be palpably wrong; indeed, an attempt to draw the figure with a bent ruler, as a continuous curve, fails utterly.

The changes of direction do not, of course, depend on thermometric differences of great actual magnitude, but their magnitude, relative to the total lowering, is considerable, and implies large alterations in the rate of change, as may be seen from the prolongation of line I. Further reference to this will be made later on.

The magnitude of these alterations is in perfect agreement with those noticed in the same region in the case of the densities and heat of dissolution; and, it may be remarked, the change at 1 per cent., which here appears to be the most doubtful one, was also very feebly shown in the case of heat of dissolution results, and was somewhat questionable in the case of the densities.

The position of the changes as indicated by the two series are—

Series 1.	Series II.
0·10 per cent.	0·07 per cent.
0·355 ,,	0·35 ,,
0·94 ,,	1·05 ,,

Series II did not extend far enough to establish the change at 1·05 per cent. very satisfactorily.

The discrepancy between 0·07 and 0·10 per cent. is not greater than might be expected from the paucity of the points in Series I, and the smallness of the actual percentage difference, but it makes a considerable difference in the molecular composition of the hydrate indicated (8000 or 5000 H_2O).

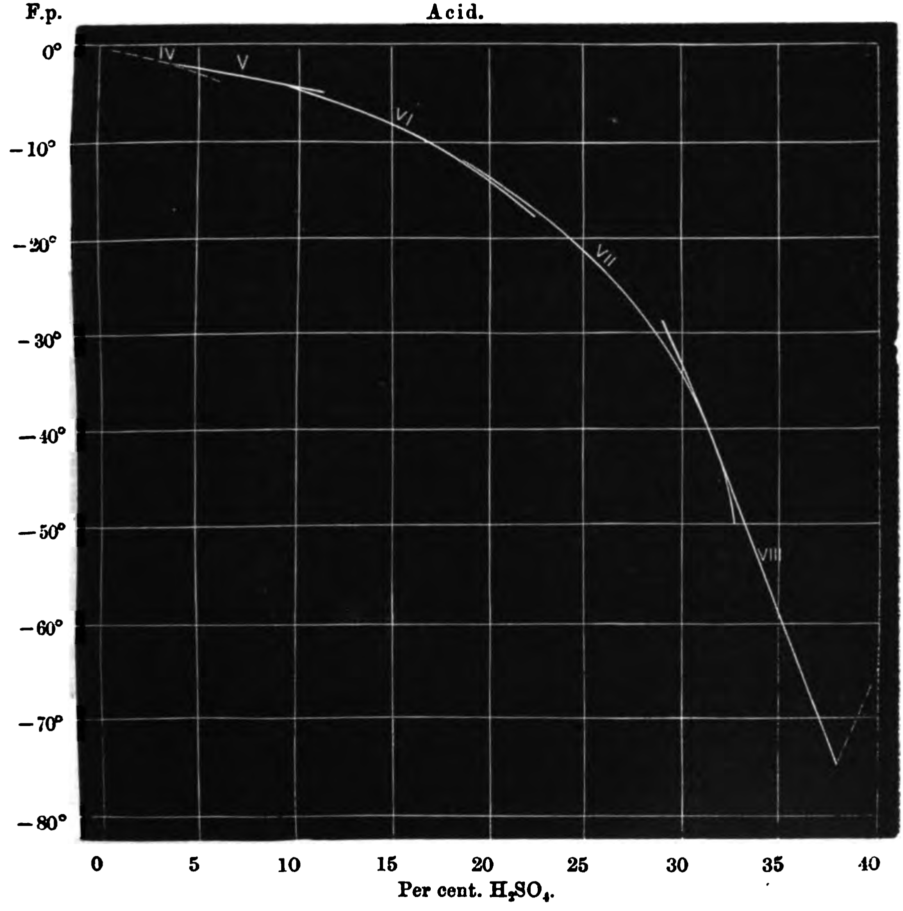
(2.) *Stronger Solutions.*

Fig. 4 illustrates the results obtained by the dissolution method with solutions from 3 to 38 per cent.

Down as far as 8 to 9 per cent., the points lie on a line which is straight within the experimental error, which is much greater here than with very weak solutions. This line is not a continuation of that representing the results with the crystallisation method from 1 to 4 per cent. (which is reproduced in IV, Fig. 4), so that some change at about 4 per cent. seems probable; but it is of such a slight character that the single dissolution determination at 3 per cent. would be insufficient to show it, and as it, therefore, must depend on the fitting together of two series obtained by different methods, it cannot be regarded as well established. It may be remarked that if line IV is straight, as is possibly the case, the last determinations at 4 per cent. in the crystallisation series will lie below this line, and will, therefore, indicate some change in this neighbourhood.

The diagram is continuous throughout; but, on drawing it with a bent ruler, it certainly does not appear to consist of a single curve; it can only be drawn in three different sections, indicating changes of curvature at about 9, 17, and 30 per cent.; but these changes, except perhaps the last, are not very well marked. The best scale on which

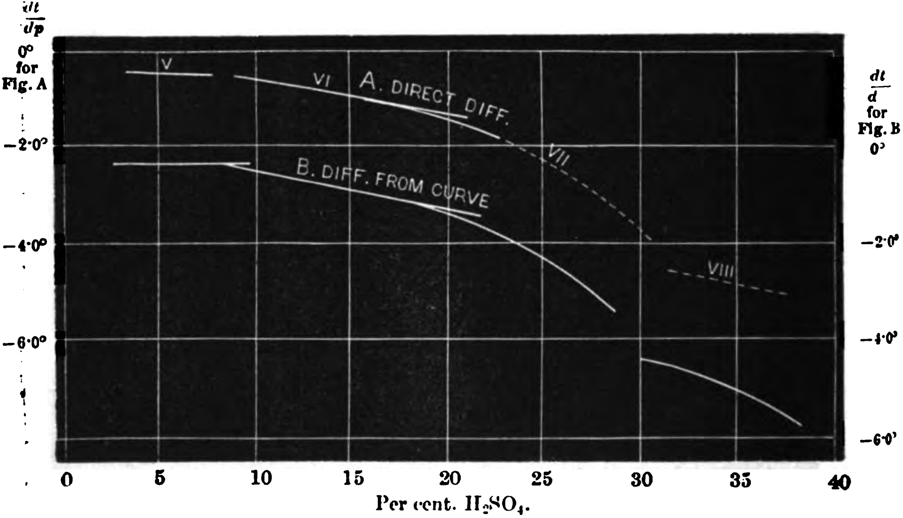
Fig. 4.—Freezing Points of Stronger Aqueous Solutions of Sulphuric Acid.



to plot these results, so as to show the changes by the application of a bent ruler, was found to be 1 per cent. and 2° to the inch, but about half a dozen other scales were tried, that which was least favourable for showing the changes being used for drawing the curve which was subsequently differentiated. Further evidence of their existence was sought: (1) by a direct differentiation of the experimental values themselves; (2) by drawing the figure as one continuous curve, smoothing out the irregularities as far as possible, and then differentiating this curve. These results are given in Tables III and IV, and are illustrated by Fig. 5, A and B. (For details as to the methods of differentiation, reference must be made to Trans., 1890, 67.)

The direct differential (in drawing which it is well to take mean points at certain places) consists of two straight lines, V and VI, followed by a curve, VII. It cannot be extended beyond 24 per cent. with any accuracy, owing to the determinations with stronger solutions being of a rough character, but the results are sufficient to indicate some considerable change in the neighbourhood of 30 per cent.

FIG. 5.—First Differentials of the Freezing Points of Aqueous Solutions of Sulphuric Acid.



The differential from the smoothed curve (Fig. 5, B) yields, of course, more regular results, but results which closely resemble those of the direct differential. The portion VIII appears to be curved.*

The changes at 9 and 17 per cent. are certainly not well marked, and depend on differences of smaller relative magnitude than those with very weak solutions. In this respect, the evidence from the freezing points coincides with that from other sources.

The positions of the changes as determined by the three methods of analysis, together with what I consider is the most probable mean, are the following:—

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* A different scale must be adopted in plotting out the values above 24 per cent. in Table IV.

Drawing with bent ruler.	Direct differential.	Differential of smoothed curve.	Mean.
8·5 p. c.	9·0 p. c.	8·5 p. c.	8·7 p. c.
16·5 „	16·0 „	19·0 „	17·2 „
30·0 „	(32·0 „)	29·0 „	29·5 „

The Tetrahydrate Curve.

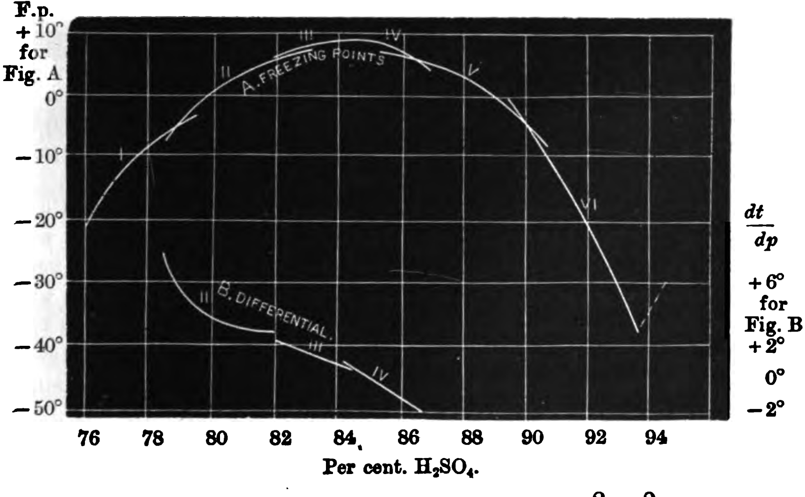
All the determinations forming this curve are of an approximate character, and are shown with sufficient clearness in the figure representing the general results (Fig. 2, p. 338).

The sudden change of curvature at the maximum, 57·6 per cent., is unquestionable. The only other hydrate which, according to my previous work, occurs in the range embraced by this curve, is that with 5·5 H_2O at 49·8 per cent. There is no certain indication of it given by any change of curvature here, but the determinations were insufficient in number and accuracy to render the existence of any such indications at all probable.

The Monohydrate Curve.

Fig. 6 represents this curve on a larger scale than was used in Fig. 2. All the determinations were made by the dissolution method. The results below −10° are of doubtful accuracy, owing to the slowness with which the hydrate dissolves.

Fig. 6.—Freezing Points of Solutions of Water and Sulphuric Acid in the Monohydrate, and Differential therefrom.



The curve is a remarkable one in many respects; the gradual manner in which the maximum (8·53°) is reached, and the sharpness of the changes of curvature on either side of it, as well as the magnitude of the two other changes at 79 and 89 per cent., being specially noteworthy. The abruptness of the change at 82 per cent. is rendered more evident by adopting a less open scale for the percentages than that in Fig. 6.

The highest portion of the figure may be drawn in various ways with a bent ruler, showing an actual discontinuity at 82 and 86 per cent., or otherwise; but, however the ruler be bent, the existence of sudden changes at these two percentages is palpable, especially at 86, where we must either represent absolute discontinuity (an improbable representation), or a well-marked re-entrant angle. In some of the possible ways of drawing this portion of the figure we get indications of a change of curvature at the apex, 84·6 per cent., in others we do not. That the monohydrate exists is unquestionable; that it exists in solution is also, I maintain, a necessary consequence of our being able to obtain it from a solution, and it appears curious, at first sight, that its existence should be marked by a change of curvature of such an uncertain nature. I applied differentiation to the smoothed curve from 82 to 79 per cent., to see if the evidence in favour of there being a change here would be thereby increased. The curve taken for this purpose was the most regular one which could be drawn: from 86 to 82 per cent., the figure was drawn in one section, without allowing any perceptible change of 84·6, and the drawing was continued in another section as far as 79 per cent., the whole figure being continuous. The readings of this curve are given in Table IV, and the differential deduced from them is depicted in Fig. 6, B.

From this we find further evidence of there being a change at 84·6 per cent., the differential from 86 to 82 per cent. consisting of two straight lines meeting at this point; but the change is by no means well marked, and is in striking contrast with the change at 82 per cent.

The uncertain manner in which the change at the monohydrate is marked is in exact concordance with a similar observation which was made as regards the other properties of the acid examined, the heat of dissolution especially. Although, wherever differentiation was applied till a rectilineal figure was obtained, I got the change at the monohydrate shown prominently, yet in all the experimental curves themselves this change was either doubtful or invisible; the freezing points add but another instance of the same character.

The two other changes which this figure shows, at 90 and 79 per cent. respectively, are of a very marked character, and require no aid from differentiation to render them apparent. They are both marked by the existence of re-entrant angles.

On plotting out the experimental values, it will be noticed that near the points where the various changes occur, the determinations have been repeated, often with different solutions.

The Sulphuric Acid Curve.

Fig. 7.—Freezing Points of Solutions of Water in Sulphuric Acid, and Differential therefrom.

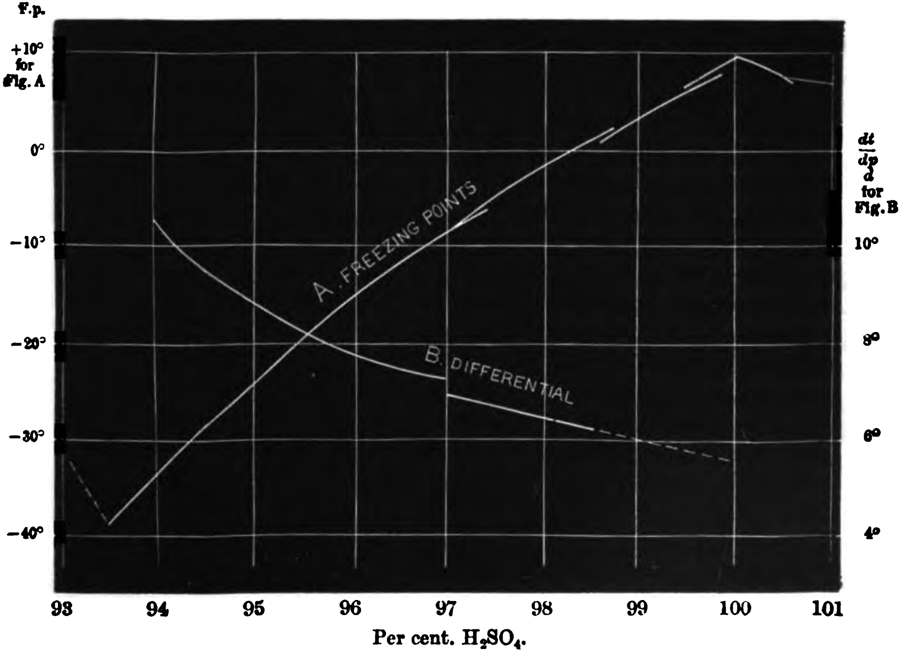


Fig. 7 illustrates the drawing made of these results. The dissolution method was the one adopted. The abruptness of the change of curvature at 100 per cent. has already been noticed. From this point down to about 97 per cent., the experimental points may be represented by a gentle curve differing but little, though appreciably, from a straight line. But to draw it as a single curve would not be admissible; such a drawing would represent seven consecutive determinations between 99·5 and 98·6 per cent. as being all too low to the extent of as much as 0·4°. The drawing here depicted follows the course of the points more closely, and indicates two changes at 98·6 and 99·5 per cent. respectively. The only doubt which I have in accepting this drawing is that it represents an apparent discontinuity in the figure. The numerous determinations near these changes were, however, made at different times, and with different solutions. The determinations at 98·03 and 97·62 per cent. are somewhat doubtful; the acid from which the solutions were made was the residue contained in a bottle which had been opened several times; the strength of them may therefore have been somewhat less than it ought to have been.

Below 97 per cent. the curvature of the figure becomes pronounced, and proceeds with regularity till it meets the monohydrate curve, the determinations at 95·08 and 95·51 alone showing abnormally large (but opposite) errors.

It was possible to draw the whole of this figure up to 100 per cent. in one section, though the drawing did not appear so consistent with the points as one which showed a change at 97 per cent. However, such a drawing was made, smoothing out the minor changes at 98·5 and 97·5 per cent., and the figure differentiated (Table IV), but the results obtained only confirmed the view that a change did exist near this point. Fig. 7, B, illustrates the differential.

The brief extension of the freezing points to solutions containing excess of anhydride was necessary to show the nature of the change at 100 per cent.; it affords an instance of a sudden change of curvature, at 100·63 per cent., of almost as marked a character as any other in the whole series. There were ten determinations made on this branch of the curve, and they are all very concordant, repetitions with the same or different solutions having been made at three points where accuracy seemed to be most requisite. The angle made by the two sections of this branch is re-entrant, and the change of curvature is therefore unquestionable.

Discussion of the Results.

The general results of the crystallisation of solutions containing between 0 and 100 per cent. H_2SO_4 prove the existence of four different solid compounds (including water and the acid itself), and, as I have argued above, of the same substances in the liquid condition.

The question which naturally suggests itself at first is, why, if there are yet other compounds, as my former work implies, do they also not crystallise out, each forming an independent curve with a rising and falling branch? The answer is obvious. Different substances, as is well known, differ widely in the ease with which they pass from the liquid to the solid condition; a solution of a composition corresponding to a definite hydrate, say, $H_2SO_4 9H_2O$, will contain not only this hydrate, but a certain proportion of its products of decomposition, and, at a given temperature, it may be supersaturated with the $9H_2O$ hydrate, and with higher and lower ones; one of these latter, although present in much smaller proportions than the $9H_2O$-hydrate, will separate out in preference to it, if it assumes the solid condition more easily. In fact, the crystallisation of a particular hydrate must be determined by the ease with which it assumes the solid condition, the relative proportions in which it is present, its solubility in the other substances present, and the temperature of its normal freezing point.

That the same solution may be supersaturated with two different substances, or that the conditions of equilibrium may be so nicely balanced that the nature of the solid added is sufficient to determine the crystallisation of either one or other compound, has been proved by Roozeboom (*loc. sup. cit.*) in the case of calcium chloride (and I have verified his observation), where solutions of certain strengths may be made to yield a crop of crystals either of the hexahydrate or of the tetrahydrate, and at different temperatures, according to which of these salts is used to touch off the solution: in fact any two main curves, such as those in Fig. 2 (p. 338), can, in the case of calcium chloride, at any rate, be produced beyond the point at which they meet. It would be useless to expect the isolation of every hydrate in the solid condition, and, unless by chance (such as touching off the liquid with a substance isomorphous with the unknown crystals), I think it improbable that any fresh hydrates will be solidified.

Their presence in solution can be revealed solely by the irregularities of changes of curvature in the main curves.

Position of the Changes of Curvature.

The various changes of curvature have been mentioned in describing the details of each of the main curves. It only remains to see whether their positions agree with those of the changes shown by the properties previously examined.

The following table contains the present and previous results, the latter being the means deduced from one to seven different cases, each case meaning the examination of a different property, or that of the same property under different conditions of temperature. The letters N.D. signify that there were no data, or not sufficient data, to determine whether the particular change existed or not. The changes which are best established are marked by an asterisk.

The concordance is most satisfactory. There is not a single change mentioned in the earlier results which has not been confirmed by this subsequent work, wherever the data obtained were sufficient;

TABLE A.—*Position (in Percentage Values) of the Changes of Curvature.*

Freezing points.	Other properties.	Composition of the definite hydrates.
1. 100·6*	N.D.	$36H_2SO_4$ SO_3 = 100·499
2. 100·0*	N.D.	H_2SO_4 = 100·000
3. 99·5	99·47	$36H_2SO_4$ H_2O = 99·493
4. 98·6	—	12 ,, ,, = 98·492
5. 97·0	97·38	6 ,, ,, = 97·444
6. N.D.	93·89	3 ,, ,, = 94·233
7. 89·8*	88·70	3 ,, 2 ,, = 89·095
8. 86·0*	N.D.	7 ,, 6 ,, = 86·403
9. 84·5	84·24	1 ,, 1 ,, = 84·488
10. 82·0*	N.D.	6 ,, 7 ,, = 82·360
11. 79·0*	78·43	2 ,, 3 ,, = 78·407
12. N.D.	73·04	1 ,, 2 ,, = 73·142
13. 57·6*	58·14	1 ,, 4 ,, = 57·656
14. N.D.	49·92	1 ,, 5·5 ,, = 49·756
15. N.D.	38·58	1 ,, 9 ,, = 37·701
16. 29·5*	29·59	1 ,, 13 ,, = 29·526
17. 17·2	18·92	1 ,, 24 ,, = 18·492
18. 8·7	8·7†	2 ,, 58 ,, = 8·585
19. 4·0	3·99	1 ,, 130 ,, = 4·021
20. 1·0	1·06	1 ,, 510 ,, = 1·057
21. 0·35*	0·34	1 ,, 1500 ,, = 0·362
22. 0·07*	0·105	1 ,, 8000 ,, = 0·068

of the four changes which have not been confirmed, three are placed near the junction of two of the main curves, where the lowness of the temperature, and the alteration in the nature of the reaction, would preclude the possibility of establishing them (in one case no freezing points at all were obtained), while the fourth is situated on the imperfectly examined tetrahydrate curve.

The average difference between the former and present results is but 0·369 per cent.; in two cases only does it exceed 1 per cent.,‡ and it is only in the last hydrate that the present work introduces any modification in the molecular composition shown by the previous results.

The freezing points show five changes which the other properties did not; two of these are in a region beyond that to which the earlier work extended; the third (98·6 per cent.) is a somewhat uncertain change, which would scarcely have been shown by any of the other properties, and, although there were not sufficient data in the earlier work to show the remaining two (at 86 and 82 per

† The actual mean was 9·69, but the more probable value was 8·7 (p. 127).

‡ Omitting these, the average difference is only 0·271 per cent.

cent.), there were facts which induced me to suggest the possibility of their existence (p. 132).

It is interesting to note that my former suggestion, that the higher hydrates contain sulphuric acid in proportions which bear simple numerical relations in the various cases, obtains further support from the present work. We have the series—

$36H_2SO_4 : 1SO_3$*
36 „ : $1H_2O$
12 „ : 1 „
6 „ : 1 „
3 „ : 1 „
3 „ : 2 „

and it will also be seen that the complex hydrates which the monohydrate forms are—

$6(H_2SO_4H_2O) : H_2SO_4$ and
$6(H_2SO_4H_2O) : H_2O$

respectively; but, as I said before, these indications must be accepted with great caution.

Nature of the Changes.

The freezing points of solutions possess certain advantages over the other properties hitherto examined for revealing sudden changes of curvature.

The results at 100 and 57·6 per cent. prove that definite hydrates are in some cases marked by undoubted changes in the curvature. This is a point of great importance. These and many of the other changes are of a much more marked character than those shown by other properties, but the lowness of the temperature may account in part, no doubt, for this. With very weak solutions, they may not be greater in magnitude than in the case of the heat of dissolution and densities, but, since the experimental figure consists of straight lines, the changes are more easily recognisable, and their position more easily determined. With stronger solutions, we get some of the changes marked so plainly—sometimes even by re-entrant angles—that a cursory inspection is sufficient to establish their existence, while in the majority of cases we have no need to have recourse to the somewhat unsatisfactory process of differentiation to render them visible.

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* The determinations did not extend far enough to determine the position of this change with any certainty.

The nature of individual portions of the main curves is probably not parabolic, as with the other properties. The first differential of the results with very weak solutions will consist of a series of horizontal lines; with stronger solutions, where the experimental curves exhibit but a moderate amount of curvature, we get a first differential which is sensibly rectilineal, while, with the rest of the figure, we get a strongly curved first differential; and repeated differentiation of such curves, I find, fails to reduce them to straight lines. In cases, therefore, where differentiation alone will reveal the changes, the freezing points will yield more doubtful results than other properties, for the true nature of the differential is not yet known.

The strict similarity between the differential of the water, the monohydrate, and the sulphuric acid curves (Figs. 5, 6, and 7) is very noticeable, the opposite direction in which the first of these bends is but the result of the experimental curve having been plotted in this case from left to right.

Another point which must make us careful in using the freezing points as a means of recognising hydrates is, that some of the changes of curvature *may* be the results of the alteration in the molecular composition of the solvent. Raoult's work has shown that water as a solvent generally acts as if its molecules consisted of $3H_2O$, sometimes of $4H_2O$; this applies to very weak solutions; and, as we increase the strength of the solution, it is possible that these complexes may simplify, inducing as a consequence, alterations in curvature. Such simplification might (and probably would) occur only coincidently with changes in the hydrates present, and, if so, it would lead us to no false conclusions, but we are at present in the dark on this point. At any rate, the simplification of the $3H_2O$ (for such the water molecule seems to be in sulphuric acid solutions) could involve but *two* sudden changes of curvature at most, while as many as *seven* have been recognised in the water curve. A simplification of the solvent molecules, it may be noted, might affect the other properties, but about this we know nothing. It *must* affect the freezing points.

Bearing of the General Results on the Theories of the Nature of Solutions.

The establishment of the sudden changes of curvature is, I maintain, conclusive against any physical theory of dissolution according to which the action must be of a regular nature. But even the more general characteristics of the freezing points give important evidence in the same direction.

If the freezing point be determined by the balancing of the three attractions of solvent for solvent molecules, solvent for dissolved molecules, and dissolved for dissolved molecules, then, when we increase the strength of the solution, we shall increase the attraction of the dissolved molecules for each other, and, therefore, lessen the relative magnitude of their attraction for the solvent molecules; the latter will be at greater liberty to combine with each other, and the freezing point of such solutions should consequently be abnormally high; the same will be the case according to the osmotic pressure theory, on which the deviations from regularity are regarded as due to the dissolved molecules being brought within the sphere of each other's attraction. But, as a matter of fact, the reverse is the case: in every instance here given, and in every other instance at present known, strong solutions give abnormally *low* freezing points, and the temperature of solidification falls at an *increasing*, instead of *diminishing*, rate, whether they are plotted out against percentage composition, or against composition expressed as so many foreign molecules to 100 molecules of the solvent. It is indeed surprising that van't Hoff, Arrhenius, and others should not have recognised that every known deviation from the so-called normal depression, when induced by increasing of strength of the solution, is in exactly the opposite direction to that in which it should be if the law of osmotic pressure were really correct. I do not mean, however, to question the applicability of this law to van't Hoff's "ideal" solutions, or to question the correctness of the conclusions which they draw from premises with which they start.

If, however, solutions contain hydrates, these, although the above cause (tending to render the depression abnormally small with strong solutions) will still exist, its influence will be counterbalanced by the dissolved substance taking away and combining with some of the water, thereby rendering the solution stronger than it would appear to be according to the relative number of H_2O and H_2SO_4 molecules present. I do not mean to state that the abnormally large depression is inexplicable on *any* physical cause, or that it *proves* the correctness of the chemical theory, but only that it is inconsistent with the physical theories of solution at present existing, while it is not inconsistent with the hydrate theory.

According to the supporters of the osmotic pressure theory, the depression of the freezing point is not only independent of the nature of the solvent and of the dissolved substance (with some numerous exceptions), but it is directly proportional to the amount of the latter present to every 100 parts of the solvent. In other words, each branch of the four different curves (Fig. 2, p. 338) should be a straight line. The deviations from straightness are too palpable to be denied, and the statement, therefore, has to be limited to solutions containing so little of the dissolved substance that the particles of this latter are as far removed from the sphere of each other's attraction as they would be if in the gaseous condition. A solution of about 0·44 per cent. strength, or $0·07H_2SO_4$ to $100H_2O$, would contain the acid in the same state of dilution as it would be when a gas at 760 mm. pressure; but the experimental facts, on which the same conclusions were based, were obtained with solutions some ten times stronger.

Now, at 2·5 per cent. the molecular depression is nearly the same as it is in the majority of cases where salts are dissolved in water: it is 2·09 (37·6),* while Raoult's average value is 2·06 (37) (Raoult's value in the case of sulphuric acid itself was 2·11 (38·2), *Ann. Chim. Phys.* **11**, 100); this point (2·5 per cent.), moreover, occupies the highest relative position in the diagram. Drawing a straight line from the freezing point of this 2·5 per cent. solution (about H_2SO_4 to $200H_2O$) to that of water, we find that the actual determinations are very far from agreeing with such a line; the maximum deviation is as much as 0·0157°, or 26 times the experimental error, and, at 0·07 per cent., it amounts to 28 per cent. of the total depression. Fig. 8 illustrates these results, and even if we draw the straight line from 0 to 0·44 per cent. (where all the actions should, according to the osmotic pressure theory, be absolutely uniform), we get a similar aberration; amounting at 0·07 per cent. to 0·0080°, or 20 per cent. of the total depression.

The alteration in the values of this so-called constant is shown by the fourth column of the following table, and its influence on the calculations for the molecular weight of sulphuric acid is shown in the last column, these values being relative ones, based on the supposition that the depression at 2·5 per cent. gives the theoretical weight.

The irregularities, even with solutions far weaker than those which, according to the theory of osmotic pressure, should behave with perfect regularity, are very great; and, although we might, from *a priori* considerations, imagine that sulphuric acid would be an exceptionally favourable instance for showing irregularities, especially in the regions of extreme dilution, yet, it must be admitted that it is an instance of typical regularity as far as somewhat rough determinations are concerned; for, not only is the depression with a solution containing one foreign molecule to $100H_2O$ identical with that observed in the majority of cases, but the action is approximately regular for a considerable distance (as far as a 10 per cent., or

---

* I use the term molecular depression to signify that which would be produced by one dissolved molecule on 100 *molecules* of the solvent; it is generally used to mean that produced by one gram molecular proportion of the dissolved substance on 100 *parts by weight* of the solvent. I give the values for the latter quantities in brackets.

e. 8.—Deviation of the Freezing Points of Weak Solutions of Sulphuric Acid from the Line of Minimum Depression.

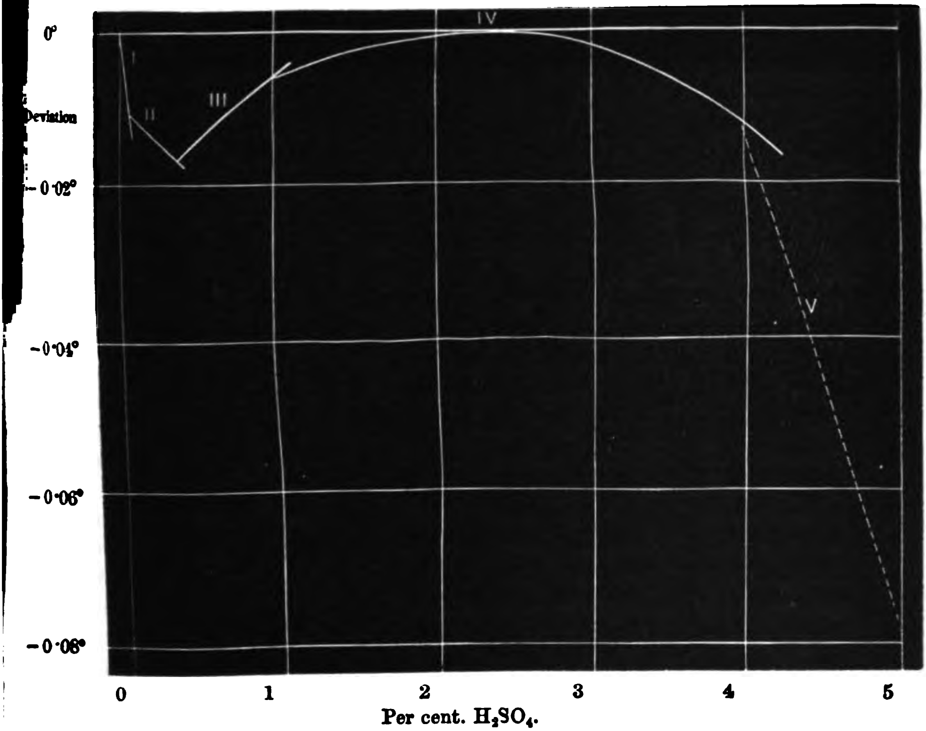

TABLE B.—*Depression of the Freezing Point of Water produced by the Addition of Sulphuric Acid.*

Per cent. H_2SO_4.	Mols. H_2SO_4 to $100H_2O$.	Freezing point.	Molecular depression.	Calc. mol. weight of H_2SO_4.
0·068	0·0125	− 0·0369°	2·95° (53·1°)	69·27
0·3618	0·0667	− 0·1580°	2·37° (42·7°)	86·14
1·057	0·1961	− 0·4214°	2·15° (38·7°)	95·04
2 500	0·4708	− 0·9825°	2·09° (37·6°)	(97·82)
4·021	0·7692	− 1·600°	2·08° (37·4°)	98·34
6·000	1·1855	− 2·520°	2·15° (38·7°)	95·04
8·585	1·724	− 3·456°	2·00° (36·1°)	101·88
18·492	4·167	−11·83°	2 84° (51·1°)	71·98
29·526	7·692	−34·00°	3·74° (67·3°)	54·65
37·701	11·111	−72·63°	6·54° (117·7°)	31·25

$2H_2SO_4$ to $100H_2O$ solution), and such irregularities as this part of the diagram exhibits would have been within the limits of the errors of any determinations which have hitherto been made. We have, therefore, no reason to conclude otherwise than that other substances will exhibit similar or even greater irregularities when investigated with a similar degree of care.

To draw an analogy between deviations of solutions from Raoult's law and the deviation of gases from Boyle's law, is, I think, out of the question. In the latter case the deviations themselves are perfectly regular, are always in the same direction, exist only in extreme cases, and are perfectly intelligible. The deviations from Raoult's law, however, have never been stated to be absent except in extreme cases where their recognition would have been impossible, owing to the comparative magnitude of the error in the somewhat rough experiments which had, so far, been made,* and, even in these extreme regions, the present work now shows that they still exist: they occur, moreover, with no regularity whatever, being sometimes in one direction, sometimes in the other, and must therefore be unintelligible on any physical theory of solution.

To base any arguments for the physical theory of solution on such a false analogy is out of the question. But it does not follow from this that the depression of the freezing point may not be still of great use as a practical method of determining the molecular weights of substances in the quasi-gaseous condition. But we must make allowance for many marked exceptions and abnormal values, and, even after doing so, we may be misled by such irregularities as have been found in the case of sulphuric acid. Great caution must, therefore, be observed in using it.

The depression of the freezing point of the monohydrate produced by the addition of sulphuric acid is abnormally small, and shows no signs of being constant throughout the whole range investigated. The following are some of the values :—

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* Indeed I am not aware of any series of determinations having been made at all to ascertain whether deviations existed or not. Some of Heycock and Neville's results with alloys may, however, be quoted as affording further illustrations of irregularity with very weak solutions (Trans., 1889, 667).

TABLE C.—*Depression of the Freezing Point of the Monohydrate by the Addition of Sulphuric Acid.*

Composition.*		Molecular depression.
84·72 p. c. H_2SO_4	H_2SO_4 to $100H_2SO_4H_2O$	0·01° (approx.)
85·12 „	$5H_2SO_4$ „ „	0·10
86·40 „	$16{\cdot}67H_2SO_4$ „ „	0·136
89·10 „	$50H_2SO_4$ „ „	0·197

Similar values are obtained for the depression produced by the addition of water, thus:—

TABLE D.—*Depression of the Freezing Point of the Monohydrate by the Addition of Water.*

Composition.		Molecular depression.
84·36 p. c. H_2SO_4	H_2O to $100H_2SO_4H_2O$	0·02° (approx.)
83·84 „ „	$5H_2O$ „ „	0·05
82·36 „ „	$16{\cdot}67H_2O$ „ „	0·12
78·41 „ „	$50H_2O$ „ „	0·31

With sulphuric acid, on the other hand, the addition of water produces an abnormally large depression, and a depression which is fairly constant.

TABLE E.—*Depression of the Freezing Point of Sulphuric Acid by the Addition of Water.*

Composition.		Molecular depression.
99·82 p. c. H_2SO_4	H_2O to $100H_2SO_4$	1·072°
99·10 „ „	$5H_2O$ „ „	1·070
97·03 „ „	$16{\cdot}67H_2O$ „ „	1·116
94·23 „ „	$33{\cdot}33H_2O$ „ „	1·253

but these values are by no means the same as those obtained in the case of the lowering produced by excess of sulphuric anhydride, where we find—

TABLE F.—*Depression of the Freezing Point of Sulphuric Acid by the Addition of Sulphuric Anhydride.*

Composition.		Molecular depression.
100·182 p. c. H_2SO_4	SO_3 to $100H_2SO_4$	0·422°
100·604 „ „	$3{\cdot}38SO_3$ „	0·582
101·024 „ „	$5{\cdot}84SO_3$ „	0·634

* The percentage of H_2SO_4 in the monohydrate is 84·4885.

With the tetrahydrate the depression is very small, and, especially where the foreign substance is sulphuric acid, very irregular.

TABLE G.—*Depression of the Freezing Point of the Tetrahydrate.*

(a.) By Water.

Composition.		Molecular depression.
57·595 p. c. H_2SO_4	H_2O to $100(H_2SO_4 4H_2O)$	0·078 (approx.)
57·353 „ „	$5H_2O$ „ „	0·073 „
54·213 „ „	$60H_2O$ „ „	0·067
49·76 „ „	$150H_2O$ „ „	0·076
45·59 „ „	$250H_2O$ „ „	0·083
37·70 „ „	$400H_2O$ „ „	0·108

(b.) By Sulphuric Acid.

57·90 p. c. H_2SO_4	H_2SO_4 to $100(H_2SO_4 4H_2O)$	0·40 (approx.)
58·84 „ „	$5H_2SO_4$ „ „	0·27
68·54 „ „	$60H_2SO_4$ „ „	0·42

Selecting from the above those values which apply to solutions containing not more than one foreign molecule to 100 of the solvent, and comparing them with the values obtained by Raoult, we get—

TABLE H.—*Molecular Depression of the Freezing Points of Various Solvents by Various Substances.*

Solvent.	Dissolved substance.	Molecular depression.
Organic liquids	Most substances investigated	0·63°
Water	Most organic substances	1·03
„	Most inorganic salts	2·06 to 2·61°*
„	Sulphuric acid	2·1 „ 2·95 †
Tetrahydrate of sulphuric acid	Water	0·08
„ „ „	Sulphuric acid	0·04
Monohydrate of sulphuric acid	Water	0·02
„ „ „	Sulphuric acid	0·01
Sulphuric acid	Water	1·072
„ „	Sulphuric anhydride	0·422

The constancy of the value is very far from apparent; in some cases it is 300 times as great as in others, and of the seven instances

* According to the salt.

† According to the strength.

investigated in the present work, there are not two in which it has the same value.*

So-called Cryohydrates.

That the so-called cryohydrates are not really definite compounds I have already contended (*Chem. News*, **52**, 239), and the present work affords some excellent illustrations in support of such a contention.

Taking the branches of any figures which represent the crystallisation of two different substances, such, for instance, as the two branches shown in Fig. 2 (p. 338) between 0 and 57 per cent., it will be seen that, if we start with weak solutions and cool them down, water will crystallise out, the strength of the solution becoming greater, and the temperature becoming lower the more we cool it, while, if we start with the stronger solutions, the tetrahydrate will crystallise out, the solution becoming weaker, in this case, as the temperature falls: between these solutions there must be one of such a strength that on cooling it, both water and the tetrahydrate will crystallise out simultaneously, leaving the composition of the liquid unaltered. This liquid (38 per cent.) will, therefore, solidify as a whole, although the solid formed will be but a mixture of two substances. In fact, a cryohydric point is the *lowest* point in any figure, while a definite compound crystallising out *must* always be situated at the highest point.

A solution at the cryohydric point is the coldest solution of the same solvent and dissolved substance obtainable, except by superfusing, and as superfusion is impossible in the presence of any of the solid itself, the temperature at this point must be identical with that obtained on mixing the crystallised solid (the tetrahydrate in this case) with ice, provided we mix the two in proportions which are not very far removed from that in which they should be mixed to form a liquid of the strength of the so-called cryohydrate.

Summary and Conclusion.

The freezing points of solutions of sulphuric acid form four separate figures, each of which represents the crystallisation of a different substance. In the case where water crystallises out, the figure consists of a single branch curve, whereas in the cases where the tetrahydrate, the monohydrate, and anhydrous sulphuric acid crystallise out, each figure consists of two curves rising up and meeting at points corresponding with the composition of the substance crystallising in each case respectively (see Fig. 2).

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* A fuller discussion of the bearing of these and other results on the theory of osmotic pressure will be found in a forthcoming number of the *Phil. Mag.*

The tetrahydrate, as a solid, is a new hydrate melting at —25°, its existence in solution having been previously established.

Irregularities and sudden changes of curvature are found in the figures. These changes occur at the same points as those noticed in the case of the densities, heat capacity, heat of dissolution, expansion by heat, and electric conductivity.

Of the seventeen hydrates indicated by the last-named properties, every one has received further confirmation from the present work where such confirmation was possible (in thirteen cases); in addition to which, three others have been recognised (two of which were, however, suggested by the previous work), thus raising the total to twenty. Sudden changes at H_2SO_4 and at about $36H_2SO_4SO_3$ have also been established.

The freezing point diagram shows that the existence of a definite hydrate may be marked by an indubitable change of curvature at the point corresponding to its composition (*e.g.*, $H_2SO_4 4H_2O$ and H_2SO_4). Many of the changes are sufficiently marked to be evident without the aid of differentiation.

The constituent portions of the various figures are probably not parabolic.

The changes at the extreme end of the water curves, with solutions containing less than H_2SO_4 to $100H_2O$, are of considerable magnitude. The figure here, instead of being made up of one straight line, is made up of several straight lines, the last change observed occurring with solutions as weak as 0·07 per cent. H_2SO_4 or $0{\cdot}0125H_2SO_4$ to $100H_2O$. The molecular depression shown, *even in this extreme region*, instead of being constant, as it should be according to the theory of osmotic pressure, varies between 2·95° and 2·1°.

The molecular depression in the various curves ranges from 0·01° to 2·95°, according to the nature of the solvent and that of the dissolved substance, these numbers referring only to solutions containing not more than one foreign molecule to 100 solvent molecules. In no two cases out of the seven investigated does it possess the same value.

In every case an increase in the strength of the solution beyond this proportion entails an abnormally low freezing point. According to all existing physical theories of solution, the freezing points of such solutions should be abnormally high.

TABLE I.—*Freezing Points of Sulphuric Acid Solutions. Crystallisation Method.*

Series I. With Thermometer 65108.

Composition.		Freezing point. Degrees C.	
Per cent. H_2SO_4.	Mols. H_2SO_4 to $100H_2O$.	Observed.	Corrected.
3·9934	·7637	(−1·6988)	(−1·6070)
3·9668	·7584	−1·6673	−1·5761
3·4915	·6642	−1·4527	−1·3724
3·0080	·5694	−1·2552 −1·2588 } 1·2570	{ −1·1860 −1·1896 } 1·1878
2·8055	·5300	−1·1668	−1·1023
2·4958	·4700	−1·0385	− ·9810
1·9956	·3739	− ·8338	− ·7878
1·7851	·3338	− ·7462	− ·7051
1·5956	·2977	− ·6699	− ·6331
1·3977	·2603	− ·5902	− ·5581
1·2124	·2253	− ·5123	− ·4844
1·0244	·1900	− ·4395	− ·4166
0·8188	·1516	− ·3529	− ·3340
0·7138	·1150	− ·3136	− ·2972
0·6145	·1135	− ·2680	− ·2546
0·5146	·0950	− ·2311	− ·2193
0·4061	·0749	− ·1868	− ·1775
0·3562	·0656	− ·1680	− ·1597
0·3063	·0564	− ·1452	− ·1382
0·2594	·0478	− ·1214	− ·1154
0·2056	·0378	− ·0999	− ·0952
0·1539	·0283	− ·0707	− ·0672
0·1401	·0258	− ·0649	− ·0617
0·1012	·0186	− ·0540	− ·0517
0·0771	·0143	− ·0401	− ·0383
0·0519	·0096	− ·0267	− ·0255
0·0264	·0049	− ·0163	− ·0157

Series II. With Thermometer 65561.

1·7957	·3357	− ·7439	− ·7026
1·5962	·2978	− ·6633	− ·6266
1·3943	·2596	− ·5810	− ·5489
1·1963	·2223	{ − ·5019 (− ·4982)	− ·4744 (− ·4709)
1·1063	·2054	− ·4663	− ·4409
1·0006	·1866	− ·4258	− ·4028
·9467	·1755	{ − ·4013 (− ·3981)	− ·3734 (− ·3704)
·8929	·1654	− ·3789	− ·3584
·8485	·1571	{ − ·3609 (− ·3661)	− ·3414 (− ·3466)

TABLE I—*continued.*

Composition.		Freezing point. Degrees C.	
Per cent. H_2SO_4.	Mols. H_2SO_4 to $100H_2O$.	Observed.	Corrected.
·7912	·1474	− ·3418 (− ·3386)	− ·2225 (− ·3193)
·7474	·1383	− ·3233	− ·3060
·6944	·1284	− ·3028	− ·2868
·6476	·1197	− ·2828	− ·2679
·5979	·1104	− ·2618 (− ·2594)	− ·2480 (− ·2456)
·5470	·1010	− ·2407	− ·2281
·4984	·0920	− ·2223 (− ·2254)	− ·2108 (− ·2140)
·4508	·0831	− ·2024	− ·2150
·4002	·0738	− ·1809	− ·1717
·3562	·0656	− ·1634	− ·1552
·3225	·0594	− ·1502	− ·1428
·2798	·0515	− ·1313	− ·1249
·2415	·0443	− ·1139 − ·1127 } − ·1133	− ·1083 − ·1071 } − ·1077
·2004	·0396	− ·0955	− ·0909
·1791	·0329	− ·0859	− ·0818
·1591	·0293	− ·0774	− ·0737
·1401	·0258	− ·0700	− ·0668
·1200	·0221	− ·0627 − ·0636 } − ·0632	− ·0599 − ·0608 } − ·0604
·0996	·0183	− ·0497 − ·0494 } − ·0496	− ·0474 − ·0471 } − ·0473
·0897	·0165	− ·0485	− ·0464
·0799	·0147	− ·0409 − ·0418 } − ·0414	− ·0391 − ·0400 } − ·0396
·0696	·0128	− ·0393	− ·0377
·0599	·0110	− ·0326	− ·0312
·0504	·0093	− ·0281	− ·0269
·0401	·0074	− ·0228	− ·0219
·0298	·0055	− ·0176	− ·0169
·0249	·0046	− ·0132 − ·0122 } − ·0127	− ·0126 − ·0116 } − ·0121
·0198	·0036	− ·0110 − ·0134 } − ·0122	− ·0105 − ·0129 } − ·0117
·0149	·0027	− ·0092	− ·0089
·0100	·0018	− ·0047 − ·0039 } − ·0043	− ·0045 − ·0037 } − ·0041
·0050	·0009	− ·0033 − ·0049 } − ·0042	− ·0034 − ·0048 } − ·0041

Table II.—*Freezing Points of Sulphuric Acid Solutions.*

Dissolution Method.

Composition.			Freezing points. Degrees C.
Per cent. H_2SO_4.	Mols. SO_3 to $100H_2SO_4$.		
Sulphuric acid crystallises out.			
101·0243	5·84	—	{6·672 6·634} 6·653
100·8171	4·62	—	7·419
100·6403	3·59	—	{8·107 8·071} 8·089
100·6038	3·38	—	8·379
100·4243.	2·40	—	9·179
100·2121	1·17	—	9·849
100·0953	0·52	—	10·155
	Mols. H_2O to $100H_2SO_4$.	Mols. $H_2SO_4H_2O$ to $100H_2SO_4$.	
100·0000	0	0	10·352
99·8826	0·64	0·64	9·617
99·7845	1·18	1·19	9·121
99·6007	2·18	2·23	8·058
99·4569	2·97	3·07	7·091
99·4132	3·22	3·33	6·786
99·2886	3·90	4·06	6·130
99·2048	4·37	4·57	5·648
99·0440	5·26	5·55	4·649
98·7913	6·66	7·14	3·032
98·7663	6·80	7·30	2·791
98·7335	6·99	7·51	2·673
98·6457	7·48	8·08	2·079
98·5625	7·94	8·62	1·900
98·5346	8·10	8·81	1·591
98·1974	10·00	11·11	− 0·413
98·0316	10·91	12·28	(− 1·676)
97·8168	12·21	13·91	− 2·883
97·6210	13·27	15·30	(− 4·345)
97·4318	14·36	16·77	− 5·349
97·0924	16·31	19·49	− 7·744
97·0257	16·70	20·05	− 8·087
96·6970	18·60	22·85	−10·407
96·1251	21·95	28·13	−14·501
96·1171	21·80	27·88	(−13·686)
95·5205	25·54	34·30	−18·275
95·160	27·70	38·32	−23·5*
94·922	29·14	41·12	−24·75*
94·597	31·11	45·15	(−28·0)*
94·278	33·07	49·41	−31·0*
94·034	34·56	52·80	−33·0*

* Observed with an alcohol thermometer.

TABLE II—*continued.*

Composition.			Freezing points. Degrees C.
Per cent. H_2SO_4.	Mols. H_2O to $100H_2SO_4$.	Mols. $H_2SO_4H_2O$ to $100H_2SO_4$.	
Monohydrate of sulphuric acid crystallises out.			
93·556	37·52	60·04	−38·0*
93·0343	40·78	68·87	−32·0*
92·027	47·19	89·35	−20·0*
		Mols. H_2SO_4 to $100H_2SO_4H_2O$.	
91·100	53·21	87·93	−12·736
90·566	56·74	76·24	−10·202
89·822	61·73	62·00	− 5·776
88·9713	67·52	48·10	− 0·576
88·0355	74·01	35·12	+ 2·768
86·7908	82·89	20·64	5·585
86·2186	87·06	14·86	6·667
85·6789	91·04	9·84	{8·125 7·932} 8·029
85·4458	92·77	7·79	8·115
84·9717	96·33	3·81	{8·466 8·470} 8·468
84·6055	99·11	0·90	{8·561 8·464} 8·513
		Mols. H_2O to $100H_2SO_4H_2O$.	
84·0050	103·71	3·71	8·404
83·3212	109·03	9·03	7·829
82·8726	112·57	12·57	7·309
82·0452	119·19	19·19	5·934
81·8494	120·78	20·78	5·441
80·6767	130·45	30·45	2·217
79·8932	137·07	37·07	{− 0·38 (− 0·12)
79·0466	144·41	44·41	− 4 486
78·9508	145·21	45·21	− 4·773
77·9908	153·70	53·70	− 8·699
76·9899	162·78	62·78	−15·199
75·8940	173·00	73·00	−22·0*
73·217	199·24	99·24	None.
71·475	217·37	117·37	"
Tetrahydrate of sulphuric acid crystallises out.			
	Mols. H_2SO_4 to $100H_2O$.	Mols. H_2SO_4 to $100H_2SO_44H_2O$.	
69·136	41·128	16·128	−54·0*
65·065	34·117	11·617	−39·0*
60·085	27·638	2·638	−28·5*

* Observed with an alcohol thermometer.

TABLE II—*continued.*

Composition.			Freezing points. Degrees C.	
Per cent. H_2SO_4.	Mols. H_2SO_4 to $100H_2O$.	Mols. H_2O to $100H_2SO_4 4H_2O$.		
56·892	24·232	12·678	−25·0*	
55·128	22·557	43·322	−28·5*	
49·725	18·160	150·07	−36·7*	
44·504	14·724	279·17	−49·0*	
39·951	12·207	419·21	−68·0*	
38·490	11·489	—	−72·0*	
Water crystallises out.				
37·662	11·092	—	−71·0*	
37·422	10·980	—	−72·0*	
35·993	10·324	—	−68·5*	
34·978	9·877	—	−61·0*	
34·874	10·295	—	−56·5*	
32·577	8·871	—	−47·0*	
29·930	7·843	—	−35·5*	
27·583	6·993	—	−28·3*	
25·787	6·121	—	−23·6*	
23·9655	5·787	—	(−19·676)	
22·9497	5·455	—	−18·075	
21·8689	5·139	—	−16·302	
21·0042	4·882	—	−14·996	
19·9007	4·562	—	−13·520	
19·2284	4·371	—	−12·700	
18·0067	4·032	—	−11·265	
17·0076	3·763	—	−10·269	
15·9399	3·482	—	− 9·111	
14·7681	3·181	—	− 8·121	
13·4851	2·869	—	(− 7·105) − 7·006	
12·7720	2·688	—	− 6·478	
11·9624	2·495	—	− 5·855	
11·0190	2·274	—	− 5·266	
9·9713	2·033	—	− 4·602	
8·9868	1·813	—	− 4·078	
7·9731	1·591	—	− 3·492	−3·430
7·9072	1·576	—	− 3·367	
6·9943	1·381	—	− 2·994	
5·9316	1·158	—	− 2·441	
5·0023	0·967	—	− 2·042 − 2·058	−2·050
4·1970	0·804	—	− 1·697 − 1·689	−1·693
3·99342	0·764	—	− 1·582	
3·0058	0·569	—	− 1·142	

* Observed with an alcohol thermometer.

TALBE III.—*Freezing Points of Sulphuric Acid Solutions.*

Direct Differentiation of the Results.

p.	*t*.	$\frac{dt}{dp}$.	*p*.	*p*.	*t*.	$\frac{dt}{dp}$.	*p*.
37·542	−71·5	−5·16	36·57	17·0078	−10·269	−1·085	16·47
35·993	−63·5	−4·47	35·47	15·940	− 9·111	−·845	15·85
34·942	−58·8	−4·99	33·76	14·768	− 8·121	−·830	14·13
32·577	−47·0	−4·34	31·25	13·485	− 7·056	−·810	13·13
29·930	−35·5	−3·07	28·76	12·772	− 6·478	−·770	12·37
27·583	−28·3	−2·62	26·69	11·962	− 5·855	−·624	11·49
25·787	−23·6	−2·15	24·88	11·019	− 5·266	−·633	10·50
23·966	−19·676	−1·576	23·46	9·971	− 4·602	−·532	9·48
22·950	−18·075	−1·640	22·41	8·987	− 4·078	−·631	8·46
21·869	−16·802	−1·510	21·44	7·940	− 3·430	−·461	7·47
21·004	−14·996	−1·388	20·45	6·994	− 2·994	−·520	6·46
19·901	−13·520	−1·220	19·56	5·932	− 2·441	−·421	5·47
19·228	−12·700	−1·175	18·63	5·002	− 2·060	−·454	4·55
18·007	−11·265	−0·997	17·51	4·095	− 1·638	−·455	3·55
17·008	−10·269			3·006	− 1·142		

TABLE IV.—*Freezing Points of Sulphuric Acid Solutions.*

Differentiation of Parts of the Smoothed Curves representing the Results.

p.	*t*.	$\frac{dt}{dp}$.	*p*.	*p*.	*t*.	$\frac{dt}{dp}$.	*p*.
			Water crystallises out.				
38	−74·3	−5·6	37·5	21	−15·02	−1·42	20·75
37	−68·7	−5·2	36·5	20·5	−14·31	−1·30	20·25
36	−63·5	−5·0	35·5	20	−13·66	−1·26	19·75
35	−58·5	−4·9	34·5	19·5	−13·03	−1·20	19·25
34	−53·6	−4·7	33·5	19	−12·43	−1·16	18·75
33	−48·9	−4·5	32·5	18·5	−11·85	−1·14	18·25
32	−44·4	−4·4	31·5	18	−11·28	−1·08	17·75
31	−40·0	−4·3	30·5	17·5	−10·74	−1·02	17·25
30	−35·7	−3·2	29·5	17	−10·23	−1·02	16·75
29	−32·5	−2·8	28·5	16·5	− 9·72	−0·96	16·25
28	−29·7	−2·8	27·5	16	− 9·24	−0·94	15·75
27	−26·9	−2·5	26·5	15·5	− 8·77	−0·90	15·25
26	−24·4	−2·30	25·5	15	− 8·32	−0·90	14·75
25	−22·10	−2·14	24·5	14·5	− 7·87	−0·84	14·25
24	−19·96	−1·86	23·75	14	− 7·45	−0·84	13·75
23·5	−19·08	−1·74	23·25	13·5	− 7·03	−0·74	13·25
23	−18·16	−1·70	22·75	13	− 6·66	−0·78	12·75
22·5	−17·31	−1·64	22·25	12·5	− 6·27	−0·68	12·25
22	−16·49	−1·50	21·75	12	− 5·93	−0·70	11·75
21·5	−15·74	−1·44	21·25	11·5	− 5·58	−0·62	11·25
21	−15·02			11	− 5·27		

TABLE IV—*continued.*

Water crystallises out.

p.	t.	$\frac{dt}{dp}$.	p.
11	− 5·27	−0·64	10·75
10·5	− 4·95	−0·62	10·25
10	− 4·64	−0·60	9·75
9·5	− 4·34	−0·58	9·25
9	− 4·05	−0·56	8·75
8·5	− 3·77	−0·54	8·25
8	− 3·50	−0·50	7·75
7·5	− 3·25	−0·48	7·25
7	− 3·01	−0·48	6·75
6·5	− 2·77	−0·50	6·25
6	− 2·52	−0·46	{6·0 to 3·0
3	− 1·14		

The monohydrate crystallises out.

p.	t.	$\frac{dt}{dp}$.	p.
86·2	+7·27	−1·55	86·1
86·0	7·58	−1·35	85·9
85·8	7·85	−1·05	85·7
85·6	8·06	−0·85	85·5
85·4	8·23	−0·65	85·3
85·2	8·36	−0·40	85·1
85·0	8·44	−0·30	84·9
84·8	8·50	−0·05	84·7
84·6	8·51	+0·05	84·5
84·4	8·50	+0·25	84·3
84·2	8·45	+0·40	84·1
84·0	8·37	+0·55	83·9
83·8	8·27	+0·75	83·7
83·6	8·12	+0·85	83·5
83·4	7·95	+1·05	83·3
83·2	7·74	+1·20	83·1
83·0	7·50		
83·0	+7·50	+1·35	82·9
82·8	7·23	+1·60	82·7
82·6	6·91	+1·70	82·5
82·4	6·57	+1·90	82·3
82·2	6·19	+2·05	82·1
82·0	5·78	+2·54	81·75
81·5	4·51	+2·64	81·25
81·0	3·19	+2·92	80·75
80·5	1·73	+3·44	80·25
80·0	0·001	+4·08	79·75
79·5	−2·03	+5·00	79·25
79·0	−4·53	+6·52	78·75
78·5	−7·79		

Sulphuric acid crystallises out.

p.	t.	$\frac{dt}{dp}$.	p.
100·0	+10·35	+ 5·75	99·8
99·6	+ 8·05	+ 5·88	99·4
99·2	+ 5·70	+ 6·13	99·0
98·8	+ 3·25	+ 6·20	98·6
98·4	+ 0·77	+ 6·35	98·2
98·0	− 1·77	+ 6·58	97·8
97·6	− 4·40	+ 6·63	97·4
97·2	− 7·05	+ 6·88	97·0
96·8	− 9·80	+ 7·43	96·6
96·4	−12·77	+ 7·45	96·2
96·0	−15·75	+ 8·00	95·8
95·6	−18·95	+ 8·30	95·4
95·2	−22·27	+ 8·70	95·0
94·8	−25·75	+ 9·38	94·6
94·4	−29·50	+10·13	94·2
94·0	−33·55	+11·00	93·8
93·6	−37·95		

XXVI.—*Contributions to the Knowledge of Mucic Acid. Part I. Hydromuconic Acid.*

By S. RUHEMANN, Ph.D., M.A., and F. F. BLACKMAN, B.Sc.

LIMPRICHT, in 1873 (*Annalen*, **165**, 253), published the results of an investigation undertaken by him with the ultimate object of ascertaining the constitution of mucic acid. The results chiefly relate to the action of bromine on hydromuconic acid and the subsequent action of silver oxide and of baryta on the brominated derivatives thus obtained. Since that time, however, no work has been done in this direction, although it would seem to be one of special interest, as probably leading to a better knowledge of the relation between mucic acid and its isomerides, especially saccharic acid, and eventually to the synthesis of these acids.

Such considerations have induced us to undertake a closer study of mucic acid. Starting from mucic acid, we first prepared chloromuconic acid, $C_6H_4Cl_2O_2$, following the directions given by Bode (*Annalen*, **132**, 195), but the yield was scarcely 25 per cent. of the weight of the mucic acid taken; the cause of this has not previously been investigated, but we are at present occupied with the problem. Chloromuconic acid is, as stated by Limpricht, very stable; the chlorine is not eliminated even by the action of boiling alcoholic potash or ammonia; aniline acts very readily on an alcoholic solution of the acid, but the crystalline product is merely the aniline salt of chloromuconic acid, $C_6H_4Cl_2O_4,2NH_2{\cdot}C_6H_5$. Analysis gave :—

	Theory.	Found.	
		I.	II.
C	54·4	54·14	—
H	4·53	5·1	—
N	7·05	—	7·05

The ethyl salt of chloromuconic acid is prepared by passing hydrogen chloride into an alcoholic solution of the acid; it crystallises in long needles which melt at 96° (Bell, *Ber.*, **12**, 1273). When heated with strong aqueous ammonia at 100°, this salt is transformed into chloromuconamide; the latter is insoluble in water and in alcohol, and decomposes when heated to about 250°. This compound is without doubt identical with the white insoluble powder obtained by Wichelhaus (*Annalen*, **135**, 251) on mixing chloromuconic chloride with ammonium carbonate. Its composition, $C_6H_2Cl_2O_2{\cdot}NH_2$, was confirmed by analysis, which gave :—

	Calculated for $C_6H_6N_2Cl_2O_2$.	Found.
N	13·4	13·37

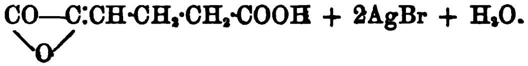
Hydromuconic acid, $C_6H_8O_4$, has already been prepared by Bode and Wichelhaus and later by Limpricht. These chemists reduced chloromuconic acid with sodium amalgam, but we find the use of tin and hydrochloric acid more convenient. On adding the acid to the reducing mixture, it dissolves; if the clear liquid be then poured off and cooled, crystals of hydromuconic acid separate, and a further crop can be obtained by concentration. It may be recrystallised from water, when it separates in long needles melting at 195°. The acid is, as Bode found, readily etherified by boiling with alcohol, but the ethereal salt is better prepared by passing hydrogen chloride into an alcoholic solution of the acid; from this it is precipitated on the addition of water as an oil which distils at 162—163° under a pressure of 35 mm. When shaken with aqueous ammonia, it gradually dissolves, but before the whole of it has disappeared, crystals separate which are readily soluble in water and yield, on recrystallisation, colourless needles melting at 210° with decomposition. A nitrogen determination showed that this substance was the amide of hydromuconic acid, $C_6H_6O_2(NH_2)_2$:—

	Calculated.	Found.
N	19·72	19·90

The composition and behaviour of hydromuconic acid indicate that it is an unsaturated dicarboxylic acid; and since it may be transformed by the action of sodium amalgam into adipic acid, $COOH{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$, its constitution must be either $COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$ or $COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$; but as Baeyer has shown that hydromuconic acid is formed by the action of sodium amalgam on diacetylenedicarboxylic acid, $COOH{\cdot}C{:}C{\cdot}C{:}C{\cdot}COOH$, the first formula must be assigned to this acid (*Ber.*, **18**, 680).

Dibromadipic acid, $C_6H_8Br_2O_4$.—By adding bromine in molecular proportion to a hot concentrated solution of hydromuconic acid in acetic acid a dibromadipic acid is formed, as Limpricht has shown. The acid, according to his statement, melts at 190° with decomposition, but on repeating this observation we found that the melting point varies between 185° and 207°, according to the rate of heating the capillary tube. This acid, as shown by the same chemist, is decomposed when treated in aqueous solution with silver oxide, losing 2 mols. of hydrogen bromide and yielding a monobasic acid, $C_6H_6O_4$, called by him muconic acid; judging from the behaviour of this acid, its formula and mode of formation must be represented as in the following equation—

$$\mathrm{COOH{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + Ag_2O =}$$



$$\mathrm{CO{-}C{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH + 2AgBr + H_2O.}$$
$$\mathrm{\underbrace{CO{-}C}_{O}}$$

From this it would be inferred that an ethereal salt of the acid could not undergo an analogous condensation; we have, therefore, investigated the action of alkalis and of ammonia on the ethyl salt of dibromadipic acid.

The ethyl salt of dibromadipic acid is readily prepared by passing hydrogen chloride into an alcoholic solution of the acid; after some time long needles separate, and on adding water the remainder of the ethereal salt is precipitated. When recrystallised from dilute alcohol, it melts at 64°, and distils at 212° under a pressure of 40 mm. with only very slight decomposition. Analysis verified its formula $\mathrm{COOC_2H_5{\cdot}CH_2{\cdot}CH_2{\cdot}CHBr{\cdot}CHBr{\cdot}COOC_2H_5}$:—

	Calculated for $\mathrm{C_{10}H_{16}O_4Br_2}$.	Found.	
		I.	II.
C	33·33	33·84	—
H	4·44	4·45	—
Br	44·44	—	44·23

This ethereal salt is formed also from ethyl hydromuconate when it is exposed to the action of bromine vapour or when bromine is directly added to it. When shaken with concentrated aqueous ammonia, it is converted into an amide, crystallising from alcohol in colourless plates which begin to decompose when heated to about 240°. This amide is free from bromine and contains two amido-groups, as analysis shows, numbers being obtained corresponding to the formula $\mathrm{C_6H_4O_2(NH_2)_2}$:—

	Calculated.	Found.	
		I.	II.
C	51·43	51·55	—
H	5·71	5·79	—
N	20·00	—	19·78

In this compound we have an amide of a bibasic acid which is formed from the ethyl salt of dibromadipic acid as follows:—

$$\mathrm{COOC_2H_5{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2{\cdot}CH_2{\cdot}COOC_2H_5 + 4NH_3 =}$$
$$\mathrm{CONH_2{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}CONH_2 + 2C_2H_5{\cdot}OH + 2NH_4Br.}$$

The acid corresponding to this amide can be easily obtained by warming ethyl dibromadipate with alcoholic potash, diluting with water, and acidifying with hydrochloric acid; a precipitate is obtained consisting of fine, white needles, which are very sparingly soluble in alcohol and in water, and decompose when heated to about 320°. Analysis shows that they have the composition $C_6H_6O_4$:—

	Calculated.	Found.
C	50·70	50·53
H	4·22	4·60

This acid is therefore isomeric with Limpricht's muconic acid, and we propose, therefore, to call it *isomuconic acid.* Finding that this isomuconic acid was so readily formed from the ethyl salt of dibromadipic acid, we tried the action of alkali on the acid itself, when we obtained isomuconic acid with equal readiness, it being necessary merely to warm it with the potash, and subsequently acidify. This experiment shows how different the action of alkalis on the bromo-acid is from that of silver oxide.

In order to further establish the constitution of isomuconic acid, we determined its basicity and analysed some of its salts. For neutralisation of 0·1617 gram of the acid, a volume of titrated potash solution containing 0·13913 gram of KHO was required; this corresponds to 54·37 per cent. of acid, the calculated percentage being 54·92. The solution of the *potassium salt*, $C_6H_4O_4K_2$, thus obtained, on evaporation yields transparent plates, which are very soluble in water but insoluble in alcohol. A potassium determination of a sample dried at 100° gave—

	Calculated.	Found.
K	35·78	35·70

Silver isomuconate, $C_6H_4O_4Ag_2$, prepared by adding silver nitrate to a solution of the acid neutralised with ammonia, is a white, insoluble precipitate which can be dried at 100° without decomposition. On analysis it gave—

	Calculated.	Found.	
		I.	II.
C	20·22	20·43	—
H	1·12	1·28	—
Ag	60·67	60·56	60·4

Lead isomuconate, $C_6H_4O_4Pb$, is prepared by adding lead acetate to a solution of the potassium salt. It is insoluble in water, and gave on analysis—

	Calculated.	Found.
Pb	60·23	60·73

Barium isomuconate, $C_6H_4O_4Ba$, was prepared by boiling isomuconic acid and baryta with water. The excess of baryta was removed by carbonic acid and the barium salt precipitated from the concentrated filtrate by alcohol. It gave on analysis—

	Calculated.	Found.
Ba	49·46	49·39

Ethyl isomuconate, $C_6H_4O_4(C_2H_5)_2$.—Owing to the very slight solubility of isomuconic acid in alcohol, its ethereal salt could not be prepared in the usual way by the action of hydrogen chloride. It is, however, readily obtained by dissolving the acid in concentrated sulphuric acid, and warming the solution with alcohol. On adding water, the ethereal salt crystallises out in colourless plates which are collected, shaken with dilute sodium carbonate to remove unaltered isomuconic acid, and then recrystallised from dilute alcohol. The crystals are very soluble in alcohol and melt at 63—64°. On analysis they gave—

	Calculated.	Found.
C	60·6	60·64
H	7·07	7·09

The formation of isomuconic acid would seem to indicate that its constitution is represented by the formula $COOH{\cdot}C{\vdots}C{\cdot}CH_2{\cdot}CH_2{\cdot}COOH$.

The action of bromine on hydromuconic acid dissolved in acetic acid is, according to Limpricht's statement, not the same as that of bromine on this acid in aqueous solution. He says that in the latter action there are formed monobromhydromuconic acid and a dibromadipic acid, which is different from the one melting between 185° and 207°, mentioned above. It seemed to us desirable to have this experiment repeated, especially as Limpricht did not succeed in isolating this isomeric acid in a pure state; and Ador (*Ber.*, **4**, 627) found that this method gave rise to a dibromadipic acid which melted with decomposition at 205°, Limpricht's impure acid melting between 115° and 120°. Following Limpricht's directions, we found that, on cooling an aqueous solution of hydromuconic acid to which, while hot, an equivalent quantity of bromine had been added, white prisms crystallised out, while long needles gradually formed in the mother liquor some hours afterwards. Examination of the substance first deposited proved that it was not, as Limpricht would have it, a monobromhydromuconic acid, but a dibromadipic acid, as stated by Ador. Moreover, comparison proved its identity with the dibrominated acid mentioned in the first part of this paper, for on heating specimens of the two acids at the same time they both melted at the same temperature (194°) with decomposition. Analysis of this acid gave numbers corresponding to $C_6H_8Br_2O_4$:—

	Calculated.	Found.
C	23·68	23·88
H	2·63	2·77

Like the acid previously mentioned, this is converted into isomuconic acid when warmed with aqueous potash. As additional evidence of identity, the ethyl salt of this dibromadipic acid was prepared and found to have the same melting point (64°) as the ethyl salt of the acid obtained by bromination in acetic acid.

The other substance which crystallises out some hours after the bromination of hydromuconic acid in aqueous solution is very soluble in water, and may be recrystallised from it in long needles which melt at 130° with decomposition. On analysis, numbers were obtained which tend to show that we have to deal here with a monobromhydromuconic acid, mixed, however, with some of the dibrominated acid:—

	Calculated for $C_6H_7BrO_4$.	Found.
C	32·28	31·65
H	3·14	3·19

Thus it would seem that by the action of bromine on an aqueous solution of hydromuconic acid, monobromhydromuconic acid and a dibromadipic acid are indeed formed, as Limpricht found, but that, in opposition to his statement, the latter acid is identical and not isomeric with the one obtained by bromination in acetic acid solution: that, further, the dibrominated acid separates out long before the monobrominated acid, although Limpricht's statement is exactly the reverse; and lastly, that the properties of melting at 120° and of crystallising with difficulty, which he associates with the dibromadipic acid, belong rather to monobromhydromuconic acid.

Note.—The above paper was already in the hands of the printer at the time we noticed the interesting work done by Rupe (*Annalen*, **256**, 1), under the guidance of v. Baeyer. Rupe has proved that the hydromuconic acid melting at 195° has the formula

$$COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH;$$

consequently, the acid we prepared and called *isomuconic acid*, and which he also obtained and named "muconic acid," has the constitution $COOH{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}COOH$.

The results of further researches in the direction indicated in the paper we hope soon to lay before the Society.

University Laboratory,
Cambridge.

XXVII.—*The Molecular Weights of Metals when in Solution.*

By C. T. Heycock, M.A., and F. H. Neville, M.A.

In a communication made to the Chemical Society, and published in the Proceedings, 1889, p. 41, we described some preliminary experiments made by us to ascertain the application of the method developed by Raoult to the case of metals in solution in each other. Since then we have continued our work in this direction, and published the results, obtained by dissolving metals in sodium (*Chem. Soc. Trans.*, 1889, 55, 666).

We now wish to bring forward the conclusion we have arrived at by using tin as the solvent. In carrying out this work we have had three chief points in view: *a.*—To ascertain how far the general conclusions arrived at by Raoult held for the solution of one metal in another. *β.*—To ascertain the atomicity (number of atoms) of the elementary molecules in solution. And *γ.*—To compare metallic solution with the solution of salts. We therefore propose to consider the work in three sections:—

A. Method of experimenting, with tables of results obtained.

B. Discussion of these results as bearing on the general theory of solution.

C. Methods of measuring accurately the temperatures we have employed.

Section A.

The experiments were made in the heavy iron blocks, as described in our paper on the lowering of the freezing points of sodium (*loc. cit.*), using paraffin on the top of the tin, in order to prevent oxidation. The molten tin was kept continually stirred by means of a water motor, and the rate of cooling of the blocks was regulated by surrounding them with asbestos cloth. The thermometers will be fully described in Section C; suffice it to say for the present that they were carefully calibrated, and would read accurately differences of temperature of 0·01° C. We may also state that, owing to the method by which the fixed points of our thermometers were determined, the temperatures given are nearly those of an air thermometer.

From an inspection of the tables, it will be seen that we have at present carried only a few of the metals to saturation; in some cases such as cadmium and lead, not given in the tables, we have found the limit of solubility, but cannot at present give the corresponding temperature until we have calibrated and determined the fixed points of our thermometers for measuring the lower temperatures.

To make it clear how the atomic falls are arrived at from our experimental values, we give a simple example. Thus in Experiment 3, Table I, silver in tin, we had a total weight of 4·3085 grams of silver dissolved in 400 grams of tin, that is, $\frac{4{\cdot}3085}{108}$ atomic weights of silver.

Hence in 100 atoms of tin we had

$$\frac{4{\cdot}3085 \times 118 \times 100}{108 \times 400} = 1{\cdot}177 \text{ atoms of silver.}$$

Now the observed freezing point of the tin was 231·68°, and of the alloy of tin and silver containing 1·177 atoms per 100 atoms of tin, 228·29°; the fall, therefore, was 3·39°. Hence the atomic fall, or fall for 1 atom per 100 of tin was $\frac{3{\cdot}39}{1{\cdot}177} = 2{\cdot}875$.

TABLE I.—*Silver in Tin.*

Expt. No.	Weight of tin in block.	Weight of silver added in succession.	Total weight of silver present.	Freezing point of solution.	Atoms of silver per 100 of tin.	Atomic fall.
	400			231·68°		
1		0·3645	0·3645	231·385	0·099	2·96
2		1·556	1·9205	230·15	0·524	2·93
3		2·388	4·3085	228·295	1·177	2·875
4		3·9012	8·2097	225·46	2·242	2·775
5		5·355	13·565	221·1	3·705	2·855
6		6·874	20·439	221·1	5·582	
7	450		„	221·1	4·962	
8	500		„	221·1	4·466	
9	550		„	221·1	4·06	
10	600		„	221·86	3·722	2·638
11	650		„	222·575	3·435	2·65

Second Series (obtained with a different thermometer from above).

	300			231·74		
1	„	2·9215	2·9215	228·626	1·064	2·927
2	„	5·317	8·239	223·555	3·00	2·728
3*	„	3·300	11·539	221·12	4·204	
4	„	1·05	12·589	221·12	4·585	
5	350		„	221·32	3·93	2·651
6	400		„	222·507	3·44	2·685
7	450		„	223·482	3·063	2·696

* Very steady temperature.

Silver prepared by Stas' method in finely-powdered, spongy condition was dropped in and dissolved easily.

TABLE II.—*Nickel in Tin.*

Expt. No.	Weight of tin in block.	Weights of nickel added in succession.	Total weight of nickel in block.	Freezing point of solution.	Atoms of nickel per 100 of tin.	Atomic fall.
	300			231·595°		
1	330	0·161	0·161	231·3	0·098	3·01
2	360	0·1855	0·3465	231·035	0·1933	2·897
3	390	0·169	0·5155	230·81	0·2655	2·957
4	420	0·1905	0·706	230·82	0·3378	
5	472·8			230·825	0 3001	
6	525·2			230·88	0·270	2·648
7	575·2			230·925	0·2466	2·717

The sample of nickel used was thin sheet, part of a crucible cover. Each quantity of nickel was kept for some time at a dull-red heat in a vacuum with weighed quantities of tin; it dissolved slowly.

TABLE III.—*Gold in Tin.*

Expt. No.	Weight of tin in block.	Weight of gold added in succession.	Total weight of gold present.	Freezing point of solution.	Atoms of gold per 100 of tin.	Atomic fall.
	200			231·8°		
1		0·2211	0·2211	231·62	0·0663	2·72
2		0·543	0·7641	231·14	0·2292	2·88
3		0·509	1·2731	230·675	0·3818	2·94
4		0·513	1·7861	230·23	0·5356	2·95
5		0·520	2·3061	229·74	0·6915	2·98
6		0·5235	2·8296	229·29	0·8686	2·89
7		1·011	3·8406	228·4	1·152	2·93
8		1·2992	5·1398	227·3	1·542	2·918
9		1·2695	6·3093	226·18	1·892	2·97
10		1·9205	8·2298	224·45	2·465	2·98
11		2·197	10·4268	222·425	3·127	2·997
12		2·2075	12·7343	220·425	3·818	2·913
13		1·5865	14·3208	219·39	4·294	2·89

The gold used was pure, obtained from Johnson and Matthey's; it dissolves at once on adding it to the tin. Unfortunately, the thermometer with which these experiments were made was broken before it was calibrated, but by a comparison of the results with other experiments we have been able to effect a partial calibration.

TABLE IV.—*Copper in Tin.*

Expt. No.	Weight of tin in block.	Weights of copper added in succession.	Total weight of copper in block.	Freezing point of solution.	Atoms of copper per 100 of tin.	Atomic fall.
	400			231·611°		
1	420	0·3118	0·3118	231·215	0·1388	2·85
2	440	1·2345	1·5463	229·692	0·657	2·921
3	460	3·646	5·2923	226·758	2·151	2·25
4	510		,,	226·758	1·94	
5	560		,,	226·758	1·767	2·746
6	610		,,	227·07	1·623	2·798

The copper was electrolytic sheet, it was dissolved like the aluminium, nickel, &c., in a vacuum. The saturated or eutectic alloy contains 1·74 atoms of copper per 100 of tin.

TABLE V.—*Thallium in Tin.*

Expt. No.	Weight of tin in block.	Weights of thallium added in succession.	Total weight of thallium in block.	Freezing point of solution.	Atoms of thallium per 100 of tin.	Atomic fall.
	400			231·543°		
1	,,	0·77	0·77	231·2	0·112	3·09
2	,,	0·7264	1·497	230·92	0·217	2·897
3	,,	1·7537	3·25	230·235	0·4707	2·778
4	,,	2·057	5·307	229·384	0·751	2·877
5	,,	3·366	8·673	228·048	1·256	2·78
6	,,	4·083	12·756	226·473	1·847	2·78
7	,,	4·751	17·51	224·619	2·514	2·754
8	,,	5·801	23·31	222·591	3·376	2·652
9	,,	4·731	28·04	220·825	4·113	2·668
10	,,	7·712	35·75	218·243	5·178	2·569
11	,,	8·723	44·47	215·555	6·44	2·483
12	,,	10·53	55·01	212·502	7·97	2·39
13	,,	9·987	64·99	210·202	9·41	2·268
14	,,	9·046	74·04	207·828	10·72	2·212
15	,,	9·631	83·67	205·415	12·12	2·155
16	,,	13·168	96·84	14·03	202·3	2·084

The alloy when poured out weighed 495·9 grams; hence the loss was 0·94 gram or 0·2 per cent.

TABLE VI.—*Sodium in Tin.*

Expt. No.	Weight of tin in block.	Weight of sodium added in succession.	Total weight of sodium present.	Freezing point of solution.	Atoms of sodium per 100 of tin.	Atomic fall.
	400			231·695°		
1	,,	1·027	1·027	227·974	1·317	2·82
2	,,	1·4285	2·456	222·708	3·15	2·855
3*	,,	1·233	3·689	220·016	4·73	2·469
4†	,,	1·475	5·164			

In these experiments the sodium was added directly to the tin, which was kept at the high temperature of 260° C., and vigorously stirred while the sodium was added. This was necessary, as otherwise a hard, infusible body was formed.

TABLE VII.—*Palladium in Tin.*

Expt. No.	Weight of tin in block.	Weight of palladium added in succession.	Total weight of palladium present.	Freezing point of solution.	Atoms of palladium per 100 of tin.	Atomic fall.
	400			231·54°		
1	450	0·125	0·125	231·47	0·0308	2·28
2	470	0·5501	0·6751	231·072	0·159	2·943
3	490	0·5725	1·2476	230·9	0·282	2·27
4	590		,,	230·9	0·234	
5	690		,,	230·995	0·2003	2·722
6	740		,,	231·02	0·1863	2·792

In Experiment 1 the palladium was a black powder which dissolved only slowly in tin at a red heat. In the other experiments palladium foil was used; when heated in a vacuum with fused tin, it became incandescent at the moment of solution.

Platinum was also tried in tin; whilst it dissolves freely at high temperatures with vivid incandesence, it appears to separate out completely before the freezing point of tin is reached.

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* Stirrer grated.

† Stirrer stuck 4° C. above last reading.

TABLE VIII.—*Magnesium in Tin.*

Expt. No.	Weight of tin in block.	Weight of magnesium added in succession.	Total weight of magnesium present.	Freezing point of solution.	Atoms of magnesium per 100 of tin.	Atomic fall.
	350			231·545°		
1	380	0·7500	0·7500	228·855	0·973	2·76
2	410	1·216	1·966	224·83	2·364	2·84
3	440	1·008	2·974	222·45	3·332	2·728
4	460	0·541	3·515	220·92	3·766	2·82
5	480	2·1355	5·650	214·97	5·803	2·856
6	500	2·1395	7·750	209·8	7·64	2·846

The magnesium alloys were made by fusing magnesium in a vacuum with small quantities of tin.

The alloys were very crystalline and attacked glass considerably.

Potassium in Tin.

Potassium in tin was tried, but the experiment failed. A hard, infusible compound was formed.

Potassium-tin alloys were afterwards made in a vacuum, but when exposed to the air at ordinary temperatures, they ignited and smouldered.

TABLE IX.—*Lead in Tin.*

Series I.

Expt. No.	Weight of tin in block.	Weights of lead added in succession.	Total weight of lead present.	Freezing point of solution.	Atoms of lead per 100 of tin.	Atomic fall.
	300			231·595°		
1	,,	0·3004	0·3004	231·445	0·0573	2·62
2	,,	0·4034	0·7038	231·23	0·1341	2·722
3	,,	0·6945	1·3983	230·878	0·2665	2·69
4	,,	0·8646	2·2629	230·39	0·4312	2·794

Series II.

	300			231·64°		
1	,,	2·828	2·828	230·135	0·5389	2·792
2	,,	2·6503	5·4783	228·835	1·044	2·687
3	,,	2·2055	7·6838	227·74	1·4643	2·663

TABLE IX—*continued.*

Series III.

Expt. No.	Weight of tin in block.	Weights of lead added in succession.	Total weight of lead present.	Freezing point of solution.	Atoms of lead per 100 of tin.	Atomic fall.
	300			231·62°		
1	„	10·269	10·269	226·56	1·957	2·56
2	„	5·353	15·627	224·75	2·978	2·307
3	„	10·485	26·112	219·58	4·976	2·42
4	„	10·935	37·047	215·31	7·06	2·31
5	„	12·3675	49·415	210·893	9·417	2·202

This experiment was continued to saturation, which occurred at 35 atoms of lead per 100 of tin.

Lead foil dissolves freely on direct addition to the fused tin.

TABLE X.—*Zinc in Tin.*

Expt. No.	Weight of tin in block.	Weight of zinc added in succession.	Total weight of zinc present.	Freezing point of solution.	Atoms of zinc per 100 of tin.	Atomic fall.
	400			231·735°		
1	„	0·326	0·326	231·36	0·148	2·54
2	„	0·3603	0·6863	230·92	0·311	2·562
3	„	0·4433	1·1296	230·37	0·5118	2·667
4	„	0·9469	2·0765	229·242	0·9409	2·65
5	„	2·8265	4·943	225·89	2·222	2·631
6	„	3·429	8·332	221·96	3·775	2·589
7	„	5·915	14·247	215·665	6·456	2·489
8	„	9·533	23·78	206·89	10·775	
9*	„	11·967	35·747	198·28	16·197	2·065
10	„	3·7096	39·457	198·28		
11	450		„	198·28		
12	500		„	200·44	14·303	2·188

Zinc dissolves like sugar in water on direct addition to the tin.

In Experiments 9 and 10 the stirrer grated considerably, long before the temperature fell to the freezing point; but as at the freezing point there was surfusion, it appears clear that zinc alone had crystallised out; otherwise there would have been no surfusion at the freezing point.

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* On ceasing to stir, the temperature rose slightly, and then was very steady.

TABLE XI.—*Cadmium in Tin.*

Expt. No.	Weight of tin in block.	Weights of cadmium added in succession.	Total weight of cadmium present.	Freezing point of solution.	Atoms of cadmium per 100 of tin.	Atomic fall.
	400			231·617°		
1	420	0·242	0·242	231·465	0·0607	2·504
2	440	0·3982	0·6402	231·235	0·1533	2·492
3	450	2·0565	2·6967	230·094	0·6314	2·412
4	460	5·209	7·906	227·295	1·811	2·386
5	470	10·034	17·904	222·465	4·0139	2·28
6	480	10·047	27·9867	218·84	6·143	2·08
7	490	10·1	38·0867	215·48	8·193	1·97
8	500	10·265	48·352	212·375	10·193	1·899

The cadmium alloys were obtained by heating weighed quantities of cadmium and tin in vacuous hard-glass tubes. The tin was saturated with cadmium, when about 47 atoms of cadmium were present per 100 atoms of tin.

TABLE XII.—*Mercury in Tin.*

Expt. No.	Weight of tin in block.	Weights of mercury added in succession.	Total weight of mercury present.	Freezing point of solution.	Atoms of mercury per 100 of tin.	Atomic fall.
	400			231·63°		
1	”	0·6175	0·6175	231·40	0·0911	2·525
2	”	0·608	1·226	231·2	0·1809	2·377
3	”	0·8945	2·120	230·893	0·3127	2·366
4	”	1·8725	3·9924	230·223	0·5889	2·377
5	”	3·3156	7·308	229·05	1·078	2·393
6	”	4·3905	11·6985	227·53	1·7256	2·376
7	”	7·0925	18·791	225·05	2·772	2·374
8	”	7·5555	26·3465	223·07	3·886	2·206
9	”	15·2845	41·631	219·395	6·141	1·998
10	”	20·813	62·44	214·62	9·21	1·846
11	”	6·9755	69·42	213·06	10·24	1·814

The addition of mercury was continued, and the fall in freezing point noted until 183 atoms of mercury were present per 100 atoms of tin; after this the surfusion ceased to be perceptible, and the experiment, therefore, was discontinued.

TABLE XIII.—*Bismuth in Tin.*

Expt. No.	Weight of tin in block.	Weight of bismuth added.	Total weight of bismuth present.	Freezing point of solution.	Atoms of bismuth per 100 of tin.	Atomic fall.
	400			231·73°		
1	"	0·1166	0·1166	231·69	0·0164	2·44
2	"	0·1939	0·3105	231·62	0·0436	2·525
3	"	0·1987	0·5092	231·55	0·0715	2·518
4	"	0·3425	0·8517	231·42	0·1196	2 592
5	"	0·6692	1·5209	231·2	0·2137	2·48
6	"	1·7922	3·313	230·65	0·4653	2·32
7	"	1·7083	5·021	230·1		
8	"	2·176	7·197	229·4	1·011	2·306
9	"	2·652	9·849	228·49	1·383	2·356
10	"	5·683	15·532	226·82	2·18	2·252
11	"	2·224	17·756	226·19	2·495	2·22
12	"	2·545	20 301	225·475		
13	"	3·458	23·759	224·43	3·34	2·136
14	"	4·865	28·624	223·03	4·02	2·17
15	"					

The bismuth dissolved easily on direct addition to the tin. The same thermometer was used as in the gold series.

TABLE XIV.—*Calcium in Tin.*

Expt. No.	Weight of tin in block.	Weight of calcium added in succession.	Total weight of calcium present.	Freezing point of solution.	Atoms of calcium per 100 of tin.	Atomic fall.
	200			231·5°		
1	230	0·0888	0·0888	231·2	0·114	2·63
2	260	0·068	0·1568	231·1	0·178	2·24

The calcium was from Harrington's, of Cork, in round lumps, very hard, and had to be cut with a cold chisel. The alloys of calcium and tin were made by heating in a hard-glass tube in a current of hydrogen. At the moment the calcium dissolves, there is vivid incandescence and a slight reduction of the glass at the point of contact. In a previous experiment the calcium was thrown directly into the block, but did not all dissolve. 0·0991 gram of calcium or 0·139 atom gave an atomic fall of 2·1 with the same minimum temperature of 231·1° as in the above experiments; hence we conclude that the solution was saturated.

Table XV.—*Indium in Tin.*

Expt. No.	Weight of tin in block.	Weights of indium added in succession.	Total weight of indium in block.	Freezing point of solution.	Atoms of indium per 100 of tin.	Atomic fall.
	200			231·585		
1	„	0·2246	0·2246	231·322	0·1178	2·24
2	„	0·202	0·4266	231·18	0·2227	1·82
3	„	0·5715	0·9981	230·64	0·5208	1·813
4	„	0·4235	1·4216	230·22	0·7423	1·839
5	300		1·4216	230·65	0·495	1·889

Indium dissolves readily on direct addition to molten tin.

Table XVI.—*Aluminium in Tin.*

Series I.

Expt. No.	Weight of tin in block.	Weights of aluminium added in succession.	Total weight of aluminum present.	Freezing point of solution.	Atoms of aluminium per 100 of tin.	Atomic fall.
	400			231·642°		
1	420	0·4805	0·4805	231·017	0·5	1·25
2	440	1·193	1·6735	229·33	1·662	1·303
3	460	0·9575	2·631	228·723	2·5	1·167
4	480	0·5	3·131	228·726	2·851	
5	530*		„	228·726	2·581	
6	580		„	228·71	2·171	
7	630		„	228·9	2·01	1·363

Series II.

	350			231·507		
	435	1·696	1·696	229·264	1·704	1·317
	445†	1·3565	3·0525	228·639	3·00	0·956
	455	0·349	3·4015	228·63	3·27	
	475‡		„	228·63		
	575		„	228·63		
	625		„	228·63		
	675		„	228·63		
	695		„	228·779	2·14	1·275
	715		„	228·852	2·08	1·275

* Temperature very steady.

† Very stationary.

‡ Raised to 278° C. before finding freezing point.

Series I.—Experiments 1 and 2 were made with thin aluminium foil; Experiments 3 and 4 were made with a new sample of aluminium from Johnson and Matthey's; purest by the sodium method.

Series II.—Johnson and Matthey's pure sheet aluminium was used. A different sample from Series I.

The aluminium was got into solution by fusing with weighed quantities of tin in hard-glass tubes in a vacuum; under these conditions, it dissolves freely at a low red heat. The rich alloys of aluminium with tin, obtained in the tubes, were brittle and friable. At the end of Series I, the paraffin above the alloy in the block appeared as a thick, white, gelatinous substance.

Other experiments, using aluminium from quite different sources, have confirmed these results.

From the foregoing experiments we conclude that, as in the case of gold and other metals dissolved in sodium (*q.v.*), the addition of a metal to tin causes a depression in the freezing point at first proportional to the weight of metal added, but that as the solution grows stronger and the volume increases, this proportion does not appear to hold (see Section II). A depression is maintained with each successive addition up to the very point when no further effect whatever is produced (see curves for zinc, Table XVIII, and for silver, copper, aluminium, nickel, and palladium, Table XVII).

The following table gives the minimum freezing point which can be obtained by dissolving in tin each of the metals mentioned:—

TABLE XIX.—*Eutectic Alloys of Tin.*[*]

Metal alloyed with tin.	Atoms per 100 of tin.	Percentages of added metal per 100 of alloy.	Freezing point.
Aluminium	2·11	0·48	228·73°
Copper	1·73	0·915	226·76
Nickel	0·26	0·13	230·82
Palladium	0·20	0·18	230·90
Zinc	15·73	7·98	198·28
Silver	4·0	3·53	221·1
Cadmium	45 (about)		
Lead	85 (about)		182° (about)

The behaviour of antimony when alloyed with tin is very remarkable, for of the seventeen metals we have examined it is the only one which behaves abnormally, namely, by its addition to tin it produces a rise in the freezing point instead of a depression (see Table XX).

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[*] An eutectic alloy (as used by Guthrie) is that particular mixture of two metals which solidifies at the lowest temperature, namely, it is the temperature at which the solvent becomes saturated with the added metal.

TABLE XX.—*Antimony in Tin. Antimony causes a Rise.*

Expt. No.	Weight of tin in block.	Weight of antimony added in succession.	Total weight of antimony present.	Freezing point of solution.	Atoms of antimony per 100 of tin.	Atomic rise.
	400			231·54°		
1		0·1437	0·1437	231·675	0·056	2·4
2		0·1640	0·3077	231·75	0·0756	2·64
3*		2·101	2·409	233·05	0·592	2·55
4		2·1694	4·578	234·23	1·126	2·39
5		2·944	7·522	235·8	1·849	2·3
6		3·1275	10·649	237·32	2·618	2·21

In Experiment 6, the stirrer worked with much grittiness towards the end.

There was very little surfusion with antimony.

Section B.

Discussion of the Experimental Results.

Our experiments lead to the following conclusions as to what takes place when an alloy is near its solidifying point. For example, taking the case of copper dissolved in tin as typical, we will consider what happens when it contains less than 0·915 per cent. of copper. As the solution cools below the freezing point of tin, pure tin crystallises out, the remaining liquid becoming more and more concentrated.† As the result, this liquid will have a lower freezing point (for freezing point is approximately proportional to the concentration). As the still liquid portion cools, pure tin continues to crystallise out at continually lower temperatures until the concentration of 0·915 per cent. is reached. At this moment copper begins to separate *pari passu* with the tin, and the concentration of the liquid does not alter, but the whole solidifies gradually at the constant temperature of 226·76°. When we start with an alloy of a concentration of 0·915 per cent. of copper in tin, it solidifies to a mass in which the copper is uniformly distributed throughout the tin;‡ a substance which is mechanically homogeneous. It is difficult to see how a solution either stronger or weaker than this can solidify slowly and remain homogeneous. The behaviour of an alloy on cooling was well shown in the case of zinc; when supersatured (above 7·98 per cent. zinc), and at a temperature above the freezing point of tin the whole alloy was liquid, but as it cooled a considerable quantity of solid matter separated out, and the stirrer scraped against the sides of the crucible as the solution solidified; at a temperature of 198·28° well-marked surfusion took place. This solid matter which separated out cannot, therefore, have been tin, or otherwise it would have acted as a nucleus and prevented all surfusion taking place. It must, therefore, be either zinc or a compound of zinc and tin; we have experiments in view by which we hope to clear up this point. The above experiments with zinc, as also many other metals, show that the solubility of metals in tin increases with the temperature as for most other cases of solution. The behaviour of a solvent in crystallising out before the substance dissolved (in dilute solutions) is taken advantage of in concentrating brine in cold climates and in the separation of lead from silver (Pattinson's method). The experiments of Roberts Austen on the regulus of Venus and other alloys also illustrate the same point. It also accounts for the capability of being moulded possessed by the solder used in "wiping" plumbers' joints.

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* Very constant temperature.

† It thus behaves exactly like a dilute solution of common salt in water when cooled below zero.

‡ In the case of gold dissolved in sodium we find on treating the alloy with alcohol, that the gold is left in the form of a spongy mass of needle-shaped crystals.

The difficulty of obtaining a plate of pure gold for a "trial plate" in the Mint is possibly due to the allied metals partially separating from the solvent as it cools.

Comparison of our Results with the Empirical Laws of Coppet and Raoult.

These laws are:—

(1.) That for moderate concentrations the fall in the freezing point is proportional to the weight of the dissolved substance present in a constant weight of solvent.

(2.) That when the falls produced in the same solvent by different dissolved substances are compared, it is found that a molecular weight of a dissolved substance produces the same fall whatever the substance is.

(3.) That if we take a constant number of molecular weights of the solvent, then the fall is independent of the nature of the solvent.

The first of these laws is well borne out by our results, as a study of any one of the tables or diagrams will show.

The second law cannot be tested without some assumption, for we had no means of deciding how many atoms of a metal form its molecule when in solution in tin. But from the fact that atomic weights of different metals produce the same fall, we might conclude that if Raoult's second law be true, then the molecules of these metals are all of the same type, say X_n, where n is the constant number of atoms in the molecule. By making the bold assumption that the molecule of zinc or of mercury is monatomic in solution in tin, as it is when in the gaseous state, one might infer that n was unity for the other metals.

Raoult's third law we found to be probably incorrect; for one atomic weight of gold when in solution in 100 atomic weights of a solvent causes a fall of about 4° when the solvent is sodium, and about 3° when the solvent is tin, and about 1·8° when the solvent is potassium. Van't Hoff has already shown that this law is false in fact and in theory (*Phil. Mag.*, 1888, **26**, 81).

Thanks to Professor Ramsay's translation of Van't Hoff's paper quoted above, we became aware, soon after we had commenced our experiments, of the theoretical explanation of the lowering of the freezing point. Van't Hoff, from the theory of osmotic pressure and the second law of thermodynamics, obtains the formula $\delta\theta = 0{\cdot}02\frac{\theta^2}{\lambda}$ for the lowering $\delta\theta$ of the freezing point when 1 mol. weight in grams of a substance is dissolved in 100 grams of a solvent. In this formula, θ is the freezing temperature of the solvent reckoned from the absolute zero of the air thermometer, and λ is the latent heat of fusion of the solvent.

The application of this formula shows that 1 mol. of any metal dissolved in 100 atomic weights of tin ought to cause a depression of 3° Centigrade in the freezing point. As this is so near the fall produced by an atomic weight of most of the metals we have examined, it seems at least very probable that the molecules of the metals are monatomic when in solution in tin (see Table of Atomic Falls, p. 392).

Professor J. J. Thomson ("Application of Dynamics to Chemistry and Physics," p. 263) has obtained by entirely different reasoning, based on Lagrange's equation of motion, but with the same assumptions as to osmotic pressure, the really identical formula $\delta\theta = \frac{\omega\theta}{\rho\lambda}$, where ρ is density of the solvent, $\delta\theta$, θ, λ have the same values as before, and ω is the osmotic pressure, that is the pressure, that the molecules of the dissolved substance are exerting inside the solution. Van't Hoff assumes and has done much to prove that this pressure obeys Boyle's, Gay Lussac's, and Avogadro's laws, and so can be easily calculated.

It is not necessary to give here a rigid proof of the above formula, but it may be worth while to indicate the kind of reasoning by which it can be arrived at.

For conciseness, let the solvent be tin and the dissolved metal gold. When the tin begins to freeze out at the temperature $\theta - \delta\theta$, pure tin freezes out, and therefore the volume in which the gold is diffused becomes smaller and work has to be done to overcome the osmotic pressure ω. If a unit volume of tin freezes out, the work done in compressing the gold is ω. Now we can find a source whence to get this work, in the liquid regarded as a perfect heat engine, for when the unit volume of tin originally melted at the temperature θ, it absorbed at this temperature an amount of (latent) heat $\rho\lambda$. When the tin froze at $\theta - \delta\theta$, most of this (latent) heat became sensible again, but a fraction $\frac{\delta\theta}{\theta}$ of the whole could, by Carnot's principle, be turned into work. That is an amount of work, $\frac{\delta\theta}{\theta}\lambda\rho$, can be got.

Equate this to the work to be done, ω,

and we get
$$\frac{\delta\theta}{\theta}\lambda\rho = \omega,$$

or
$$\delta\theta = \frac{\theta\omega}{\lambda\rho},$$

where $\delta\theta$ is the fall in temperature that must take place before the necessary work can be obtained.

In the case of a solution of 1 mol. weight of any metal in 100 atomic weights of tin we have the following constants:—

The freezing point of tin = 231·5° C.
= 504·5° absolute.
$\lambda =$ 14·25 thermal units (Person)
$=$ 14·25 × 41·6 × 10^6 dynes.
$\rho =$ 7·29.
Sn = 118.

Then the volume of a solution containing 100 atomic weights of tin is $\frac{11 \cdot 8}{\rho}$ litres, and the temperature of freezing may be taken as 500°, so that the osmotic pressure caused by the presence of one molecular weight of a foreign metal is given by

$$\omega = \frac{\Pi \times 22 \cdot 3 \times 500 \times \rho}{11 \cdot 8 \times 273} = 3 \cdot 46\,\Pi\rho,$$

where Π is the atmospheric pressure which equals 1013 × 10^3 dynes.

Substituting these values in the formula $\delta\theta = \frac{\omega\theta}{\rho\lambda}$, we find that $\delta\theta = 3°$ Centigrade.

This number is so nearly equal to the fall produced by 1 *atomic* weight of most of the metals examined as to make it very probable that their molecules, when in dilute solution in tin, are monatomic.

Professor Ramsay (Trans., 1889, **55**, 521), by his experiments on the vapour pressure of solutions of metals in mercury, and G. Tammann,* by experiments similar to ours but using mercury as the solvent, have arrived at the same result.

The atomic falls obtained for aluminium are so nearly half the average atomic falls that it seems probable that the molecule of aluminium when in solution in tin consists of 2 atoms.

To show this, we have in the diagram plotted the falls of aluminium on double the scale of the other metals.

We think that this method might be applied as a control for atomic weights, similar to that afforded by Dulong and Petit's law of specific heats.

The freezing points are so definite that they might, with advantage, be used for giving fixed points on thermometers.

Van't Hoff's formula cannot be applied to more concentrated solutions, but perhaps J. J. Thomson's might be so applied.

To do so, we must bear in mind that ω varies as $\theta - \delta\theta$ and not as θ, and also that the volume of the solution is getting larger than the volume of the original solvent. To find the total volume, we must find by experiment the density of the liquid alloy. We hope to determine these densities and so trace the changes in the atomic falls and in the osmotic pressure in concentrated solutions.

In order to obtain from the observations the most probable value of the atomic fall in dilute solutions, it seems best to add together all the total falls below the freezing point of tin, to add together all the fractions of an atom of the dissolved metal used, and to divide the first sum by the second.

Thus in the case of thallium in tin, the experiments in which the concentration was less than 1 atom of thallium in 100 atoms of tin were:—

	Atoms, f. p.	Falls below f. p. of tin.
	0·1115	0·345° C.
	0·2168	0·628
	0·4707	1·308
	0·7510	2·159
Totals.	1·55	4·44

Then $\frac{4·44}{1·55}$ = 2·86° C. is the mean.

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* "Zur Konstitution der Legierungen," *Zeitschrift für physikalische Chemie*, III Band, 5 Heft.

We *add* the falls because each is liable to the same absolute error in the temperature.

The following table has been calculated as above from the experimental results under 1 atom :—

Atomic Falls for a Concentration of under one Atom.

I.	Nickel............	2·94	3 experiments.
	Silver	2·93	2 ,,
	Gold	2·93	6 ,,
	Copper	2·91	2 ,,
	Thallium	2·86	4 ,,
	Sodium	2·84	2 expts. concn. 1—3 atoms.
	Palladium	2·78	4 experiments.
	Magnesium........	2·76	1 ,,
	Lead	2·76	8 ,,
	Zinc..............	2·64	4 ,,
II.	Cadmium	2·43	3 experiments.
	Mercury	2·39	4 ,,
	Bismuth	2·40	6 ,,
	Calcium...........	2·40	2 ,,
III.	Indium	1·86	5 experiments.
	Aluminium........	1·25	1 ,,

With the exception of calcium, where the error may be large, there can hardly be an experimental error of 5 per cent. in these, and we should think that in most cases it is much less.

In a few cases, by taking a stronger solution than 1 atom per 100, it would be possible to bring the numbers more together, for example, the atomic fall for magnesium increases to 2·86°, if not more. Similarly, aluminium increases to 1·4°. Antimony causes a rise of about 2·5° per atom, but this may be due to other causes and have no connection with the other numbers ; at all events, we do not see how, on theoretical grounds, this rise can be explained.

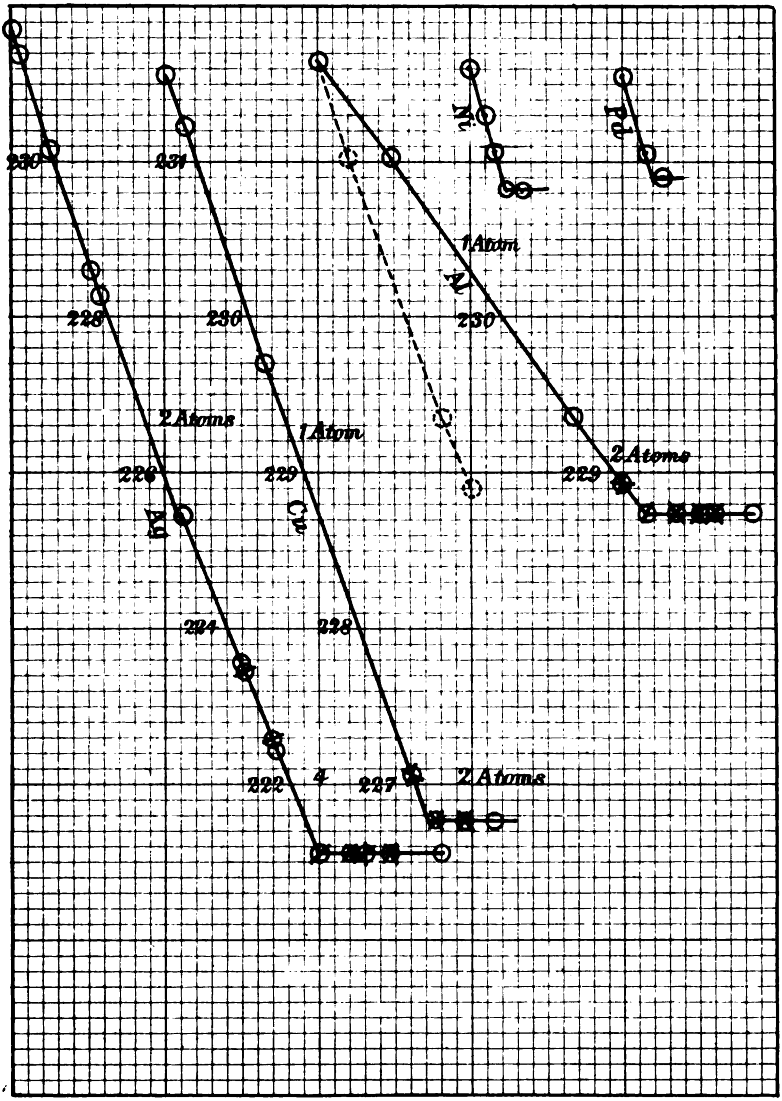
It seems clear that the nature of the metal in solution has some effect on the fall, although the atomic falls for Group I are so near the theoretical molecular fall of 3° as to make it seem very likely that their molecules are monatomic in solutions in tin.

It is curious that cadmium, mercury, and to some extent zinc, whose molecules in the gaseous state are believed to be monatomic, should give falls abnormally low, as if there were some condensation in these cases.

The case of indium suggests partial condensation, and that of aluminium strongly suggests diatomic molecules.

Journ. Chem. Soc. May 1890. HEYCOCK & NEVILLE.

PLATE 1.
METALS SPARINGLY SOLUBLE IN TIN.



THE DIAGRAM SHOWS THE TEMPERATURE AT WHICH SOLUTIONS OF DIFFERENT CONCENTRATIONS BEGIN TO FREEZE. NUMBERS ON THE LEFT ARE CENTIGRADE TEMPS. THE DOTTED LINE FOR ALUMINIUM CORRESPONDS TO A MOLECULAR WEIGHT OF 54. POINTS MARKED WITH A CROSS WERE OBTAINED BY ADDING TIN TO THE SATURATED ALLOYS.

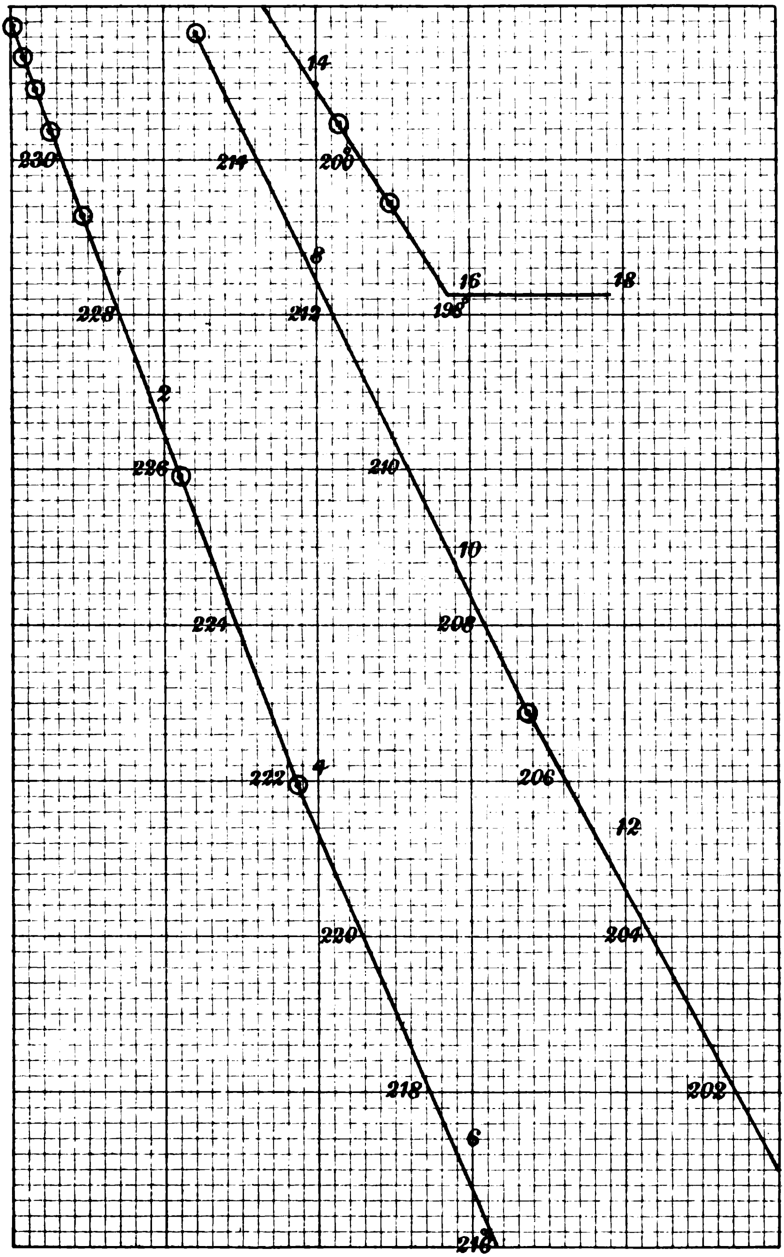
HARRISON & SONS, LITH. ST MARTINS LANE, W.C

Journ. Chem. Soc. May 1890

HEYCOCK & NEVILLE.

PLATE 2.

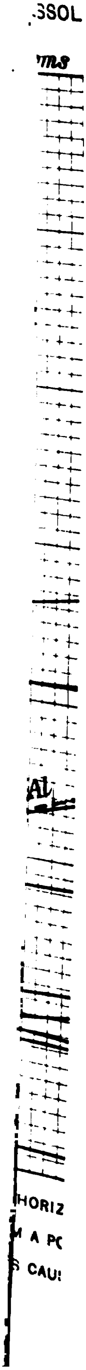
ZINC IN TIN.

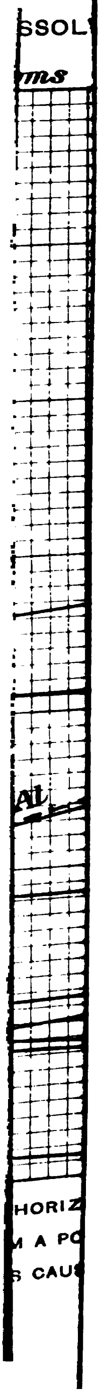


NUMBERS ON THE LEFT HAND SIDE OF THE CURVE ARE CENTIGRADE TEMPERATURES.

NUMBERS ON THE RIGHT ARE THE NUMBER OF ATOMS ZN. PRESENT PER 100 ATOMS OF SN.

HARRISON & SONS LITH. ST MARTINS LANE, W.C.


SSOL
ms
Al
HORIZ
A PC
CAU


SSOL
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HORIZ
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S CAU

The cases of gold, magnesium, and aluminium, in which the atomic fall seems really to rise or remain constant with increasingly concentrated solutions, probably point to the appropriation of some of the tin by the dissolved metal, as in the formation of hydrated salts, but until we have determined the densities of the liquid alloys, it is not possible to calculate the theoretical value of the osmotic pressure with sufficient accuracy to discuss this.

(*To be continued.*)

Sidney College Laboratory,
Cambridge.

XXVIII.—*The Formation of Indene-derivatives from Dibrom-α-naphthol.*

By **Raphael Meldola**, F.R.S., and **Frank Hughes**.

The present research originated in the course of a study of the tri-derivatives of naphthalene undertaken with the object of ascertaining whether in homonucleal tri-derivatives of the series α_1, β_2, α_4, the hydrogen-atom of the unsubstituted β_3-position could be replaced by the NO_2-group. Failing this, the possibility occurred that a heteronucleal nitrodibromonaphthol might be formed or, in view of the readiness with which dibrom-α-naphthol passes into quinone-derivatives (Meldola, Trans., 1884, 156), that a bromoquinone might be produced. Our experiments with respect to the introduction of the NO_2-group into the β_3-position have hitherto been unsuccessful (compare Prager, *Ber.*, 1885, 2158; Meerson, however, by nitrating triacetyldiamidonaphthol, has succeeded in introducing the NO_2-group into the position stated, *Ber.*, 1888, 1197), but a special study of the action of fuming nitric acid upon dibrom-α-naphthol has resulted in the discovery that in this compound the 10-carbon-atom naphthalene-ring is easily broken down into the 9-carbon-atom indene-ring.

Indonaphthene or indene (C_9H_8) is a hydrocarbon which has not yet been isolated, although many of its derivatives are known.* It was named by Baeyer and Perkin (*Ber.*, 1884, 122; also W. H. Perkin, jun., Trans., 1888, 1), in order to indicate its relationship to naphthalene on the one hand and to indole on the other. It is related to naphthalene in the same way that indole is related to quinoline. Carboxylic derivatives of hydrindene were described by

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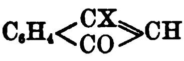
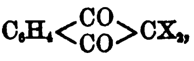
* Methylindene, $C_{10}H_{10}$, has been isolated by Roser (*Annalen*, **247**, 159).

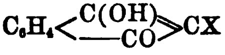
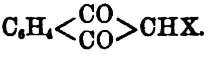
Baeyer and Perkin in the paper referred to, and later by Scherks (*Ber.*, 1885, 378). Indene-derivatives were also prepared synthetically by Roser (*Ber.*, 1887, 1273 and 1574), and investigated more thoroughly by this author (*Annalen*, **247**, 29), and by Roser and Haselhoff (*ibid.*, 138). Important contributions to our knowledge of these compounds have also been made recently by W. Wislicenus, and by this author and Kötzle (*Annalen*, **246**, 347, and **252**, 72). Hydrindone was prepared last year by the hydrolysis of ethylic orthocyanobenzylacetate by Gabriel and Hausmann (*Ber.*, 1889, 2017), and the compound in question studied in detail by the last-named author (*ibid.*, 2019).

The indene-derivatives referred to in the foregoing papers have been prepared by synthetical methods from compounds containing a smaller number of carbon-atoms than indene itself, or by condensation with ring formation from compounds containing the same number of carbon-atoms as indene. Our knowledge concerning the formation of indene-derivatives by the breaking down of the naphthalene-ring is at present derived almost entirely from the researches carried on in the laboratory of the University of Marburg by Professor Zincke and his assistants and students. Thus, in 1884, Kronfeld obtained a compound by the bromination of amidonaphthaquinoneimide, which was doubtless a derivative of indene (*Ber.*, 1884, 715). Dichloroketoindene was subsequently obtained by Zincke by the action of alkali upon dichloro-β-naphthaquinone and the oxidation of the acid-product (*Ber.*, 1886, 2500, and 1887, 1265; Zincke and Frölich, *Ber.*, 1887, 2053). Numerous other papers on these compounds from the Marburg laboratory will be found throughout the *Berichte* for the last three years.

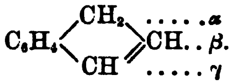
The indene-derivatives thus far obtained by the breaking down of the naphthalene-ring or by other methods are dihaloïd derivatives of ketoindene (indone) and diketohydrindene of the types:—


$$C_6H_4<\begin{matrix}CX\\CO\end{matrix}>CH$$
and

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CX_2,$$

or haloïd hydroxyketo-derivatives of the types:—


$$C_6H_4<\begin{matrix}C(OH)\\ \underline{\quad\;}CO\end{matrix}>CX$$
or

$$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>CHX.$$

As the method discovered by us gives rise to a simpler haloïd derivative of indone than has hitherto been obtained, viz., monobromindone, we thought it desirable to follow up the investigation in order to contribute to the knowledge of this little-known group of compounds. The mode of formation of our compound, moreover, enables us to start with an indene-derivative of which the constitution can be inferred with considerable certainty, and we have therefore been enabled to follow its transformations with the most satisfactory results, so far as concerns the constitution of other indene-derivatives. Throughout this paper we propose to adopt the nomenclature of W. Wislicenus and Roser (*Annalen*, **247**, 132), which is expressed by the formula:—



$$C_6H_4\begin{matrix} \diagup CH_2 \diagdown \ldots\ldots\alpha \\ \qquad\quad CH..\beta. \\ \diagdown CH \diagup\!\!\diagup \ldots\ldots\gamma \end{matrix}$$

Preparation of Dibrom-α-naphthol.

The preparation of dibrom-α-naphthol by bromination in acetic acid (Biedermann, *Ber.*, 1873, 1119) is apt to lead to bad results in the way of yield unless certain precautions are observed. We have, therefore, thought that it might be of use to other workers if we gave the details of the process found to give the most successful results. 50 grams of α-naphthol are dissolved in 250 c.c. of glacial acetic acid, and the theoretical quantity of bromine dissolved in 50 c.c. of glacial acid is gradually poured into the α-naphthol solution, kept cool by standing the vessel in water. The solution must be well shaken after each addition of bromine.. When the whole of the latter has been poured in, the contents of the flask becomes semi-solid from the separation of a mass of white crystals of an additive-compound. But little hydrogen bromide is evolved at this stage. On warming the contents of the flask, the additive-compound dissolves and decomposes with copious evolution of hydrogen bromide. The solution must be kept warm (not actually boiling) for some hours, till the evolution of hydrogen bromide has practically ceased, the decomposition of the additive-compound being finally completed by the addition of a few grams of zinc-dust, and allowing the solution to cool with occasional agitation. When cold, the solution is filtered into a large volume of cold water, and the dibrom-α-naphthol allowed to separate out; it is then collected, washed with water, and dried, being sufficiently pure for the present purpose without further crystallisation. If these precautions are neglected, the additive-compound, which may be a keto-bromide (Zincke, *Ber.*, 1888, 1036), reacts with the dibrom-α-naphthol already formed as soon as the product is precipitated with water, and a coloured compound is formed, whilst the yield of dibrom-α-naphthol is seriously diminished. By this method of working, 100 grams of α-naphthol give about 196 grams of the dibrominated derivative, instead of 209·7, that is, about 93 per cent. of the calculated yield. After being once crystallised from alcohol, the compound melts at 105—106° (Fittig and Erdmann, *Annalen*, **227**, 242).

Action of Nitric Acid on Dibrom-α-naphthol.

The action of nitric acid on dibrom-α-naphthol varies according to the strength of the acid and the conditions of the experiment. By repeatedly evaporating dibrom-α-naphthol with dilute nitric acid, it is well known that phthalic acid is obtained. If the dibromo-derivative is added to ordinary strong nitric acid (sp. gr. 1·42) in the cold, the substance gradually liquefies to an oil, which, on standing, and especially on being stirred or agitated, solidifies to a crystalline mass. The latter appears to be an additive-compound, as on exposure to the air it gives off bromine. By treatment with alkali it is resolved into a mixture consisting apparently of dinitronaphthol and nitrobromonaphthol, but the products have not yet been completely investigated. Fuming nitric acid at once converts dibrom-α-naphthol into an indene-derivative.

Preparation of γ-Brom-α-indone.

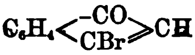
In order to prepare this compound, the dry dibromo-derivative is thrown, in small portions at a time, into well-cooled fuming nitric acid (sp. gr. 1·5); 20 grams of dibrom-α-naphthol require about 140 c.c. of acid to furnish the best results. It is not absolutely essential to use ice to cool the water in which the vessel is placed, although this precaution is to be recommended in warm weather. As soon as all the dibrom-α-naphthol has been added, the solution is allowed to stand for half-an-hour, and is then poured into a large bulk of cold water. On standing for 12 hours, the bromindone settles down as an ochreous, sandy precipitate, which is collected and washed with water till free from acid. From 20 grams of dibrom-α-naphthol, there are obtained about 14 grams of the crude indone, instead of 13·8 as required by theory, so that the yield is practically quantitative.

The crude bromindone is purified by crystallisation from alcohol, and then once or twice from glacial acetic acid. When pure, the compound forms small, ochreous scales melting at 127—128°. Heated a little above its melting point, it decomposes suddenly, so that for analysis it was found necessary to mix the substance with a large quantity of cupric oxide in order to insure uniformity of combustion. The following results were obtained:—

I. 0·1702 gram gave 0·3242 gram CO_2 and 0·0468 gram H_2O.
II. 0·1148 „ 0·2183 „ „ 0·0348 „
III. 0·1268 „ 0·1146 „ AgBr.

	Calculated for C_9H_5BrO.	Found. I.	II.	III.
C	51·68	51·94	51·84	—
H	2·39	3·05	3·37	—
Br	38·28	—	—	38·45

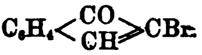
The hydrogen is somewhat high for the calculated formula, but this is doubtless due to the necessary use of cupric oxide, with which the substance has to be mixed for the reason stated. Before this precaution was taken a lower result was obtained, viz., 2·79 per cent. H. Monobromhydrindone, C_9H_7BrO, requires 3·31 per cent. of hydrogen, but from its mode of formation it is extremely improbable that our substance should have this formula. With respect to the constitution of the bromindone, two formulæ are conceivable :—



$$C_6H_4<\begin{matrix}-CO-\\CBr\end{matrix}>CH$$

I.

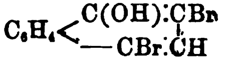
and



$$C_6H_4<\begin{matrix}CO\\CH\end{matrix}>CBr$$

II.

Taking into consideration the constitution of the dibrom-α-naphthol from which the indone-derivative is obtained, the first of these formulæ must be regarded as the more probable. The constitution of the naphthol-derivative has been shown to be



$$C_6H_4<\begin{matrix}C(OH):CBr\\ \quad\;\; | \\ —CBr:CH\end{matrix}$$

(Meldola, Trans., 1884, 161). Since the whole of the substituted ring is broken down and reconstructed with the elimination of one CBr-group and one hydrogen-atom, the constitution of the bromindone will be determined by the position of the residual CBr-group. From general considerations as to the manner in which aromatic compounds break down on oxidation, there can be but little doubt that the external CBr-group would be removed in preference to the CBr-group attached to the unsubstituted benzene- (phenylene) ring to which the two external carbon-atoms are attached in the ortho-position. For these reasons we consider formula I as the more probable. We have as yet no direct evidence respecting the nature of the product resulting from the removal of the CBr-group, but it is probably a methane-derivative, such as $CBr(NO_2)_3$ or $CHBr(NO_2)_2$. No gas is evolved when dibrom-α-naphthol dissolves in cold fuming nitric acid, and the acid solution, when diluted with water to precipitate the bromindone, always has an odour suggestive of bromopicrin. Other oxidising agents, such as chromic acid in glacial acetic acid, also furnish bromindone when allowed to act on dibrom-α-naphthol, but the yield is not so good as when nitric acid is used.

During the purification of the crude bromindone by crystallisation from alcohol, there is invariably left a small quantity of a yellowish insoluble compound, which on crystallisation from boiling glacial acetic acid, forms long, slender, yellowish needles having no definite melting point, but darkening and decomposing at about 260°. The compound is very insoluble in all solvents, requiring a large volume of boiling glacial acetic acid in order to bring it into solution for crystallisation. The yield of this substance is too small to enable us to do more than submit it to a preliminary examination. It appears to contain no bromine, and analysis points to the formula of a naphthaquinone. On reduction with zinc-dust in glacial acetic acid, and precipitation with water, it furnishes a substance crystallising in minute, white needles having no definite melting point, but blackening about 220°. It is possible that this insoluble residue resulting from the action of nitric acid on dibrom-α-naphthol may be the unknown γ-naphthaquinone (periquinone) of which a nitro-derivative has been obtained by Quincke (*Ber.*, 1888, 1454). It is hoped that sufficient of the substance will be obtained in the course of further work to enable this point to be decided.

Bromindone is freely soluble in hot alcohol and glacial acetic acid; also in cold benzene, chloroform, and acetone. It is somewhat less soluble in cold ether and carbon bisulphide. It separates rather slowly from its hot solutions on cooling. Petroleum dissolves it but slightly in the cold, but more readily on heating, the solution on cooling depositing the substance in the form of ochreous, stumpy prisms with pointed extremities, collected into stellate groups. When heated cautiously in a dry test-tube, the substance distils and partly sublimes, leaving a slight carbonaceous residue, and condensing in the cold part of the tube in an unaltered condition.

Action of Aniline on Bromindone.

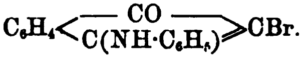
In accordance with the ketonic character of the compound, it forms coloured compounds with amines, some of which are well defined crystalline substances.

On dissolving bromindone in the smallest possible quantity of boiling alcohol and adding aniline in molecular proportion, the solution becomes of a deep brownish-orange; after boiling for a few minutes, the solution is allowed to cool, when deep orange-red, scaly crystals separate. After being allowed to stand for some hours, the crystalline deposit is collected and washed with cold alcohol. A specimen was purified for analysis by crystallisation from boiling alcohol, glacial acetic acid, and benzene successively. The pure compound forms deep-red scales melting at 190°. The analyses showed that the compound was formed by the combination of aniline with the indone without the removal of oxygen or bromine:—

I. 0·1440 gram gave 0·3140 gram CO_2 and 0·0424 gram H_2O.
II. 0·1650 „ 0·3624 „ „ 0·0498 „
III. 0·2032 „ 7·8 c.c. moist N at 13° and 748·8 mm. bar.
IV. 0·1024 „ 4 „ „ 13° „ 772·9 „
V. 0·1732 „ 0·1092 gram AgBr.
VI. 0·1740 „ 0·1095 „

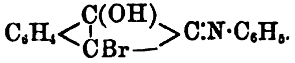
	Calculated.		Found.					
	$C_{15}H_{12}NOBr$.	$C_{15}H_{10}NOBr$.	I.	II.	III.	IV.	V.	VI.
C	59·60	60·00	59·47	59·90	—	—	—	—
H	3·97	3·33	3·27	3·35	—	—	—	—
N	4·63	4·66	—	—	4·48	4·69	—	—
Br ...	26·49	26·66	—	—	—	—	26·83	26·78

The anilide dissolves but very sparingly in boiling alcohol, the solution being red and depositing the substance, on cooling, in the form of red scales which, under the microscope, are seen to consist of broad, flattened needles. The solution in hot glacial acetic acid is orange. It dissolves readily in benzene and chloroform, and in strong sulphuric acid with a magenta-red colour. This anilide is of a different type from the compound melting at 170° obtained by Roser and Haselhoff by the action of aniline on dibromindone (*Annalen*, **247**, 148), and to which they assign the formula—



$$C_6H_4<\genfrac{}{}{0pt}{}{CO}{C(NH\cdot C_6H_5)}>CBr.$$

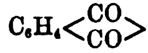
The anilide obtained by us possesses a distinctly acid character, dissolving in hot aqueous alkali with a violet colour, which soon disappears owing to the decomposition of the substance. It dissolves also with great readiness in cold alcoholic soda with an intense violet colour. The compound is decomposed by alkalis with the formation of an acid substance which is described later on in this paper. One product of decomposition under these circumstances appears to be phenyl isocyanide, the powerful odour of which is evolved whenever the substance is brought into contact with alkaline solutions. Taking into consideration the circumstances (1) that this anilide is formed by the direct combination of aniline and bromindone without the elimination of bromine or oxygen, (2) that the compound is acid and may therefore contain hydroxyl, and (3) that the grouping $:C:N-$ is present, as shown by the formation of an isocyanide under the influence of alkalis, we conclude that the most probable formula of the new compound is—



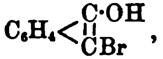
$$C_6H_4<\genfrac{}{}{0pt}{}{C(OH)}{CBr}>C{:}N\cdot C_6H_5.$$

When treated with zinc-dust in acetic acid solution, the anilide is converted into a whitish hydride which, on exposure to the air, becomes red and is oxidised back into the original compound. The hydride probably contains the group $\equiv CH\cdot NH\cdot C_6H_5$. We have not yet succeeded in acetylating or alkylating the anilide.

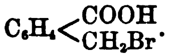
In order to obtain further evidence respecting the constitution of the anilide, the acid product of its decomposition by alkalis has been prepared and examined. The same acid product is obtained on decomposing the anilide either by alkali or by dilute sulphuric acid; prolonged boiling is, however, necessary in the latter case, and we have at present restricted ourselves to the alkaline decomposition. On boiling the anilide with dilute caustic soda, a violet solution is first obtained, the colour of which soon changes to a reddish-orange. In about 15 to 30 minutes the whole of the anilide is decomposed, leaving only a slight tarry impurity. A strong odour of isocyanide is evolved during the whole course of the decomposition. It is advisable not to prolong the boiling after the whole of the anilide has undergone decomposition, as the acid itself is liable to be decomposed on prolonged boiling with alkali. As soon as the red crystals of the anilide have disappeared, the hot solution is filtered, and the filtrate made acid with hydrochloric acid. An orange, crystalline precipitate is gradually thrown down, but the solution still contains a large quantity of the acid products, and it must be allowed to stand for at least 12 hours before the crystalline deposit is filtered off. The crude acid, when collected, is washed with cold water, dissolved in cold dilute ammonia, filtered, and reprecipitated by acid, this treatment being repeated till the ammoniacal solution leaves no residue on filtration. The acid is slightly soluble in boiling water, and advantage was taken of this property to purify specimens for analysis. It was found most advantageous to dissolve the acid in a large volume of water by the aid of a few drops of ammonia, and to heat the solution to boiling. On acidifying with hydrochloric acid and filtering hot, the acid slowly separates out on cooling in the form of dull, orange, stumpy needles melting at 191—192°.

The mode of formation and the properties of this acid lead to the conclusion that it may be a bromhydroxyindone. A compound of this nature has already been obtained by Zincke by dissolving the dibromodiketone,  $C_6H_4{<}\substack{CO\\CO}{>}CBr_2$, in alkali (*Ber.*, 1888, 2395), and by Roser and Haselhoff, by the action of caustic soda on dibromindone (*Annalen*, **247**, 149). Our substance agrees with that described by the authors referred to in dissolving in alkalis with a red colour, but it differs in melting point (191° instead of 119°), and in other respects. Thus, the acid obtained by the German investigators shows a tendency to pass into products of higher melting points (polymerides ?) on crystallisation. The acid obtained by us shows no such tendency, and the different preparations always had the same melting point whatever solvent was used for crystallising the substance.

Although we have but little doubt that this acid is a bromhydroxyindone, we have had the greatest difficulty in getting a specimen sufficiently pure to give good results on analysis. It is probable that other products of decomposition result from the action of alkali on the anilide, and, in fact, if phenyl isocyanide is produced, as appears to be the case, this indicates the partial breaking down of the 9-carbon-atom-ring into an 8-carbon-atom compound, possibly a derivative of orthophenylene-acetylene or of benzoic acid. The formula of the anilide indicates that such compounds might be formed:—



$$C_6H_4 < \begin{matrix} C\cdot OH \\ \| \\ CBr \end{matrix} ,$$



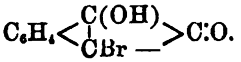
$$C_6H_4 < \begin{matrix} COOH \\ CH_2Br \end{matrix} .$$

Our study of the action of alkali upon the anilide will be continued with the special object of ascertaining what other products result from the decomposition. That the acid above described has the composition of a bromhydroxyindone is shown by the following analyses:—

I. 0·1241 gram gave 0·2184 gram CO_2 and 0·0307 gram H_2O.
II. 0·1410 „ 0·1186 „ AgBr.
III. 0·1977 „ 0·1655 „ „

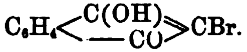
	Calculated for $C_9H_5BrO_2$.	Found. I.	II.	III.
C	48·00	47·99	—	—
H	2·22	2·84	—	—
Br	35·55	—	35·79	35·36

According to these results and from its mode of formation, the acid may be regarded as having the constitution—



$$C_6H_4 < \begin{matrix} C(OH) \\ | \\ CBr\ — \end{matrix} > C{:}O.$$

The isomeric compound of Zincke and Roser and Haselhoff has the formula—



$$C_6H_4 < \begin{matrix} C(OH) \\ —\ CO \end{matrix} \gg CBr.$$

The acid is readily soluble in alcohol, ether, and acetone, less soluble in benzene, and almost insoluble in petroleum. Heated in a dry test-tube, it partially sublimes in small, yellow needles. The silver salt is an amorphous, red powder, which is precipitated on adding silver nitrate to a solution of the ammonium salt free from excess of ammonia. More characteristic is the barium salt, which is formed by boiling the acid with water and barium carbonate; carbon dioxide is evolved and a red solution obtained, which, after filtration and cooling, deposits a mass of slender, orange needles. According to our analyses, this salt contains a large quantity of water of crystallisation, which is only partially expelled at 140—150°.

I. 0·4237 gram (dried in a vacuum over calcium chloride and heated in the water-oven till constant) lost 0·0247 gram = 5·83 per cent.

The loss calculated for $(C_9H_4BrO_2)_2Ba,7H_2O - 2H_2O = 5{\cdot}06$ per cent. According to this, the salt contains 7 mols. of water, of which 2 are expelled on heating. At a higher temperature (140—150°) the loss is not much greater: 0·5679 gram lost 0·0335 gram = 5·90 per cent.

II. 0·3990 gram (dried in a water-oven and decomposed by boiling with dilute HNO_3 and adding H_2SO_4) gave 0·1360 gram $BaSO_4$.

III. 0·5344 gram (dried at 140—150° and decomposed as before) gave 0·1822 gram $BaSO_4$.

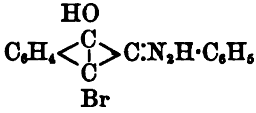
	Calculated for $(C_9H_4BrO_2)_2Ba,5H_2O$.	Found.	
		II.	III.
Ba..........	20·28	20·05	20·04

IV. 0·2940 gram (dried in a vacuum over $CaCl_2$) gave 15·53 gram AgBr.

	Calculated for $(C_9H_4BrO_2)_2Ba,7H_2O$.	Found.
Br	22·50	22·48

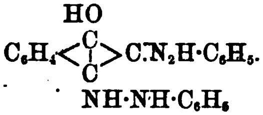
On adding aniline to the solid acid, it dissolves with evolution of heat, and red, crystalline scales separate. After purification by washing with alcohol and crystallising from the same solvent, the substance was obtained in the form of bright-red crystals which appeared under the microscope to consist of elongated hexagonal tablets. The compound proved to be the aniline salt of the acid, and not an anilide as, from its appearance, we at first regarded it. It fuses at 169°, and froths up and decomposes at 172°.

By the action of phenylhydrazine on the acid, two compounds appear to be formed, a hydrazone and a hydrazonehydrazide. On adding phenylhydrazine to the alcoholic solution of the acid, a deep orange-yellow colour is produced. If the solution is boiled for a few minutes, and then set aside to cool for some hours, a substance crystallising in small, reddish-brown needles is deposited, whilst the solution contains another compound, which is thrown out on diluting with water and adding dilute hydrochloric acid. Our examination of these products is not yet complete, and experiments will be resumed in this direction, as we anticipate that further light will be thrown upon the constitution of the acid by a study of the action of phenylhydrazine upon it. The constitution assigned to the acid indicates the existence of the two compounds :—



$$\begin{matrix} & HO & \\ C_6H_4 < & \overset{C}{\underset{C}{|}} & > C{:}N_2H\cdot C_6H_5 \\ & Br & \end{matrix}$$

and



$$\begin{matrix} & HO & \\ C_6H_4 < & \overset{C}{\underset{C}{|}} & > C{:}N_2H\cdot C_6H_5. \\ & NH\cdot NH\cdot C_6H_5 & \end{matrix}$$

The action of other amines on monobromindone has been studied in a preliminary way, but the compounds thus far obtained are by no means so satisfactory to deal with as the above-described anilide. Phenylhydrazine reacts almost explosively with the dry compound; in alcoholic solution, a deep magenta-red colour is developed, and a deposit consisting of small, bronzy scales slowly separates after many hours' standing. This hydrazone melts at about 180—182°, but we have not yet prepared sufficient of the substance for analysis, as the yield is very small.

The benzylamide is produced on adding benzylamine to the cold alcoholic solution of the bromindone. A deep yellowish-orange colour is at once developed, and on standing, orange needles separate. After crystallisation from alcohol, the substance forms orange-brown, flat needles of a silky lustre; these melt at 154°.

I. 0·1569 gram gave 5·9 c.c. moist N at 14° C. and 770·6° mm. bar.
II. 0·1256 „ 0·0745 gram AgBr.

	Calculated for $C_9H_5BrO{:}N\cdot C_7H_7$.	Found.
N	4·46	4·55
Br	25·47	25·20

The benzylamide is much more stable than the anilide, as it resists boiling with dilute acids and alkalis. It is insoluble in aqueous alkali, but its acid character is shown by the readiness with which it dissolves in cold alcoholic soda, the solution being yellow and the compound being precipitated in an unaltered condition by acids.

The β-naphthylamide was obtained in the form of minute, reddish-brown (microscopic) needles, by boiling the alcoholic solution of the bromindone with β-naphthylamine for a few minutes and then allowing the mixture to remain for several hours. It melts at about 151°, but the melting point is difficult to observe, as the compound shrinks and darkens before this temperature is reached:—

0·1330 gram gave 4 c.c. moist N at 11° C. and 770·7 mm. bar.

	Calculated for $C_9H_5BrO\colon N\cdot C_{10}H_7$.	Found.
N	4·00	3·62

The naphthylamide dissolves in cold alcoholic soda with production of a violet coloration, and in strong sulphuric acid with a similar coloration, the latter solution becoming red and the substance being precipitated unaltered on dilution with water.

Finsbury Technical College.

XXIX.—*The evidence afforded by Petrographical Research of the occurrence of Chemical Change under great Pressure.*

By J. W. Judd, F.R.S., F.G.S., Professor of Geology in the Normal School of Science and Royal School of Mines.

There is only one way in which the inevitable and ever-increasing tendency towards extreme specialisation in scientific research can be prevented from bringing about a condition of affairs injurious to scientific progress. The cultivators of different branches of science must maintain a constant, a friendly, and a helpful intercourse; each must be ready from time to time to examine the methods pursued by his fellow workers in other fields of study, and to compare notes with them as to the results obtained. The greater the divergency between the methods followed in two departments of science, the stronger becomes the necessity for such intercourse between the cultivators of them, and—I think it may be added—the more hopeful the results which are to be anticipated as being likely to follow from mutual suggestion and healthy discussion.

Chemistry may justly boast that her foundations are laid in direct experiment. Geology—though by no means neglecting experimental initiative and verification, where such are possible—is compelled for the most part to rely upon very different methods of investigation. But while the geologist may lament that he is not more often able to avail himself of experimental processes of inquiry, he may fairly ask the chemist to give due weight to results that have been obtained by perfectly legitimate, if very different, methods from his own.

In order to study the processes of development going on in an oak tree, we might plant an acorn and watch the changes that take place through a long series of years. But I am by no means sure that equally satisfactory results would not be arrived at by a visit to an oak-thicket, where innumerable examples of the plant in every stage of growth could be examined and compared. Our command of high temperatures, of intense pressures, and, above all, of *time*, to permit the factors of change to produce their slowly cumulative results, may altogether prevent our imitating many of the processes going on in the earth's crust. But a study of the rocks, and of the crystals of the minerals of which these rocks are built up, in every stage of development, and at the same time of the conditions under which these crystals have made their appearance and continued their growth, may lead us to absolutely conclusive results concerning the causes which have operated in their formation.

The application of the microscope to the study of minerals and rocks in thin, transparent sections has, during the last 30 years, greatly contributed to the advance of this kind of inquiry. It is to our countryman, Mr. Sorby, that we are indebted for calling attention to the value and importance of this method—one which is now being developed and extended by the labours of investigators in every part of the globe.

I propose to give a summary of the results that have been obtained by this method bearing upon the question of how far chemical change is induced or modified by pressure.

That at very moderate depths in the earth's crust the materials of which it is composed are subjected to great pressure is obvious, and that at considerable depths this pressure must become enormous, and far surpass what we can imitate by experiment, admits of no doubt.

The effects of pressure in the waters of the ocean have been recently investigated by Professor P. G. Tait, and his conclusions are of a very startling character. In spite of the extremely slight compressibility of water, he has shown that the parts of the ocean which are 6 miles in depth, have their surface lowered 620 feet by the pressure of the superincumbent mass. By this action the *average* level of the ocean is depressed 116 feet, and about 2,000,000 square miles of land, which would be submerged beneath the ocean if sea-water were absolutely incompressible, are now uncovered ("*Challenger*" *Reports, Physics and Chemistry*, **2**, 1889).

But the rocks composing the earth's crust have a density 2½ times as great as that of sea-water, and this density increases as we go downwards. So greatly, indeed, must the pressure in the earth's interior exceed all those which we can possibly ever hope to produce artificially, that it seems almost idle to quote the numerical results arrived at by mathematicians. Von Waltershausen calculated the pressure at the earth's centre as 2,500,000 atmospheres (*Ueber die Vulkanischen Gesteine in Sicilien und Island*, 1853), while the Rev. O. Fisher, employing Laplace's law of density, has estimated it at no less than 3,000,000 atmospheres (*Physics of the Earth's Crust*, 2nd ed., 1890).

But by far the grandest effects of pressure within the earth's crust are found to be displayed as the results of those tremendous movements that have given birth to the materials composing mountain chains. It can be shown that under great deforming stresses, slowly applied, solid rock-masses have behaved in the same way as viscous bodies, and have actually been made to *flow* like the ice of a glacier or the solid iron in Tresca's presses; brittle minerals like quartz and calcite, yielding to the internal strains set up in the rocks, have sometimes been crushed as in a mill; but have more frequently —in obedience to the irresistible forces applied to them—undergone other changes, resulting eventually in complete recrystallisation and the formation of new chemical compounds.

It may naturally be asked, at the outset, if the microscope has revealed to us any evidence of the action of such great and abnormal pressures having acted upon the minerals composing rock-masses; and to this question an affirmative answer may be given without the smallest hesitation.

It is impossible to examine the crystals composing the rocks which have once been deeply seated in the earth's crust without being struck by one peculiarity: such crystals are seen by the aid of the microscope to be crowded with minute cavities, which are sometimes present to the number of many millions to the cubic inch. Careful study of these has shown that among the substances with which these cavities are wholly or partly filled are various supersaturated aqueous solutions, and carbon dioxide in a liquefied condition. The identity of the last-named substance has been demonstrated beyond the possibility of doubt by the independent researches of Sorby and Butler, and of Vogelsang and Geissler. By the determination of its critical point, by the measurement of its coefficient of expansion, by the examination of its spectrum, and even by isolation and ordinary methods of analysis, the fact that the liquid imprisoned in these cavities is none other than carbon dioxide is placed beyond controversy. I need not stop to remind you of the wonderful and seemingly spontaneous movements of the bubbles in these cavities—movements of which the causes have been investigated by Professors Hartley and Stokes.

Let us endeavour for one moment to picture to our minds the conditions under which carbon dioxide came to be imprisoned in these crystals. A long series of observations has established the fact that temperature increases with depth in the earth's crust; the average amount of this increase can be scarcely less that 1° C. for every 30 metres of depth; and the remarkably interesting boring of Schladebach in Prussian Saxony which was completed last year, and *was carried to a depth of considerably more than a mile,* is of particular interest as proving that the temperature gradient continues remarkably constant at the greatest depths yet attained. We can scarcely doubt, therefore, that when the carbon dioxide was imprisoned in these crystals it must have been far above its critical point (31° C.), but nevertheless in such a condition of condensation by pressure, that on the rocks being exposed at the surface and submitted to ordinary atmospheric temperatures it becomes a liquid, which nearly fills the cavity in which it is enclosed.

Other and not less striking evidences of the pressures to which rock-masses and the minerals composing them have been subjected meet us at every turn in our study of rocks by the aid of the microscope. Minerals are found to be strangely deformed, and all their optical properties have in consequence undergone the most extreme modification. Owing to peculiarities in respect to cohesion in different directions which characterise crystalline substances, they have yielded, in the most remarkable manner, to the various stresses to which they have been subjected, and in consequence exhibit complicated series of fractures and twinning. Sometimes the whole mass has been ground to powder as though subjected to the action of a gigantic mill.

Two attempts have been made to calculate the actual pressures to which rock-masses been have subjected; both of these methods being based on the study of the liquid enclosures in the minerals composing the rocks.

Sorby, and after him Clifton Ward, have pointed out that if the relative volumes of the liquid and gas bubble in a cavity can be measured, we have the means of determining the temperature and pressure at which the crystal containing the cavity was formed. It may be assumed that originally the liquid or gas entirely filled the cavity, and if we can calculate the temperature and pressure at which this would take place, we arrive at the conditions under which the crystal must have been formed. But, unfortunately, we know far too little of the coefficient of expansion of aqueous solutions at very high temperatures and under extreme pressures—especially near their critical points—to hope for any satisfactory result from this method.

Professors Renard and De la Vallée Poussin have sought to attain the same object by determining the temperature and pressure at which the crystals of sodic chloride, and other salts found in the aqueous solutions contained in cavities of crystals, would pass into solution; and thus they hoped to arrive at the conditions under which the super-saturated solution existed when first sealed up in the cavity. But here, too, it must be admitted that our knowledge of the increase of solubility of salts at high temperatures is insufficient to serve as a basis for such calculations.

It is not necessary in this place to review at length the *direct experimental investigations* which have been carried on with the object of determining how far chemical action can be induced or modified by pressure.

The method of sealing up substances in glass tubes with water, and exposing them to high temperatures, has been most successfully employed by Daubrée and other French chemists and mineralogists. Glasses, both natural and artificial, which are amorphous mixtures of various silicates, were found to break up under these conditions, and their various constituents crystallised out as quartz, sanidine, wollastonite, diopside, and other well-known mineral species. In this way, a very considerable proportion of the minerals composing the earth's crust have been artificially prepared; the crystals, though of microscopic dimensions, presenting all the distinguishing characteristics of the natural ones.

But it may be, and indeed has been, objected to this method, that it is quite impossible to discriminate between the effects due to high temperatures and those which result from pressure. Bunsen has argued that at ordinary temperatures the most enormous pressures are capable of producing little effect (*Annalen der Chemie und Pharmacie*, **65**, 1848, pp. 70—85). But it was subsequently shown by Sorby that the negative results arrived at by Bunsen could be explained by the circumstance that a sufficient amount of time was not allowed for the reactions to take place (*Proc. Roy. Soc.*, **12**, Bakerian Lecture for 1863, p. 541), and it is now, I think, generally admitted that where solution is attended with contraction, the action of pressure always promotes solvent action.

It is a fortunate circumstance that, in the method adopted by Professor W. Spring of Liége, we have a series of experimental researches in which the effects of pressure have been studied *apart from those of high temperature.* In these experiments, pressures estimated to exceed 7,000 atmospheres were employed, and the precaution was taken of applying the force so slowly that any heat generated by compression would be dissipated gradually, and would, therefore, not interfere with the result. The conclusions at which Spring arrives are as follows:—

1. Powders of metals and other solids may, by intense pressure (especially if all interstitial air-films are removed by action *in vacuo*); be converted into masses undistinguishable from those produced by fusion. In powders and amorphous (colloid) substances alike, structures as completely crystalline are developed by pressure as those resulting from fusion and slow cooling.

2. Where a substance is capable of assuming different allotropic forms, the less dense may be converted into the heavier form by pressure. [Van't Hoff and Reicher (*Etudes de dynamique chimique, Amsterdam*, 1884, p. 198), have since shown that by pressure the temperature at which these paramorphic changes take place can be modified.]

3. Powders of metals, oxides, and salts may by pressure be made to react chemically upon one another, and to produce alloys or other compounds.

Professor Spring is careful to point out that these results take place in consequence of the particles of the solid bodies being brought into actual contact—their molecules within chemical striking distance as it were. He has lately pointed out several new results which are of especial interest to geologists.

4. When the grains of solid bodies are made to *rub* or *slide* over one another, the conditions are particularly favourable for chemical action being set up between them. Professor Thorpe, in 1881, called particular attention to this kind of action. He showed that when the dry powders of two anhydrous salts were rubbed together in a mortar, double decomposition takes place between them.

5. When the particles of powders have once been brought into close contact by pressure, the chemical reactions between them go forward even when the pressure is removed. Experiments carried on during four years have shown how a chemical reaction can complete itself under these circumstances: time admitting of slow diffusion between the molecules (*Zeitschrift für Physik u. Chemie*, 1889).

6. Lastly, Professor Spring has investigated the influence of the presence of small quantities of water in promoting or retarding the welding action of pressure. He has shown that where diminution in volume accompanies solution, the presence of water facilitates the solidification of powders by pressure; but, in the much rarer cases, in which increase of volume by solution takes place, the presence of water hinders solidification.

It would be impossible to exaggerate the importance of these results or to over-estimate the influence which they must have upon geological thought and speculation.

Scarcely less important and suggestive are the results arrived at by the late Dr. Guthrie, who, by a series of experiments on solution under pressure, has shown, in the case of nitre and other substances, that there is *perfect continuity between the states of solution and fusion.*

I will now pass to the evidence afforded by the microscopical study of rocks, as to results which have been produced on their constituent crystals by the enormous pressures to which they have been subjected. I must at the outset ask to be allowed to make a distinction between the different ways in which pressure can be shown to have operated upon rocks.

All the rocks situated at considerable depths in the earth's crust must be subjected to great pressure resulting from the weight of the superincumbent masses. Under these pressures, liquids and gases may be made to penetrate between the molecules of the solid crystals. The evidence that such permeation of solid crystals by liquids and gases has taken place is overwhelming. In the words of Van der Waals, "all bodies can mix with one another when the pressure exceeds a certain value."

Now these pressures, resulting from the weight of overlying rock-masses, may be called "statical pressures," and any changes or "metamorphism" produced in the rocks by this agency may be called "statical metamorphism."

But rocks have in many cases been subjected to pressure of a very different character. During the differential movements within a rock-mass resulting from folding, crumpling, and shearing—actions which go on to such an extent during mountain-making—the great stresses give rise to internal strains, and these to resultant movements that affect powerfully every constituent crystal of the rocks. Pressures such as these, operating to produce movement and work, may be distinguished as "*dynamical* pressures," and geologists have agreed to call the metamorphism which results from them "dynamical metamorphism."

It is of course not necessary to point out that, while statical pressures only effect a change in the *conditions* under which the various chemical forces act, dynamical pressures resulting in movement may, by generating heat, or in other ways, themselves become active agents in chemical change. Mr. Sorby has even argued that under the conditions which exist within the earth's crust there can be a *direct* conversion of mechanical into chemical force, and it may be that, as he argued, certain phenomena familiar to geologists will have to be explained in this way (*Proc. Roy. Soc.*, **12**, 538).

The effects produced by statical and dynamical pressures are, however, so constantly found exhibited in the same rock-mass, that any attempt to dissociate them—except for purposes of study—seems to me to be neither practicable nor desirable.

I propose to lay before you a series of propositions, the truth of which it appears to me can be established by studying the results of processes going on in the great subterranean laboratories of our earth's crust. In these laboratories more or less elevated temperatures and various solvents have operated under the conditions of enormous pressure and practically unlimited time. By the removal of the thousands of feet of superincumbent materials through denudation, the remarkable bodies produced in these laboratories are now exposed at the earth's surface for our study. As the wearing away of these enormous masses of material has required long periods of time, most of these products that we study are of great, many of them of enormous antiquity; but it sometimes happens that precisely similar bodies from the deeper parts of our earth's crust are brought to the surface during volcanic eruptions, and these serve to show that the same processes are in operation within the earth's crust at the present day.

I. *In all those cases in which crystallisation is accompanied by contraction, the tendency of pressure is to promote the change from an amorphous to a crystalline condition.*

Spring has shown that under a pressure of 6,000 atmospheres plastic or amorphous sulphur, having a density of 1·95, passes into rhombic, crystallised sulphur, having a density of 2·05.

The mixtures of silicates which constitute the igneous rocks of the earth's crust all undergo *contraction* in passing from the amorphous (vitreous) to the crystalline condition. This is easily proved by comparing the specific gravities of more or less crystalline rock-masses with that of the glasses formed by their artificial fusion. The experiments of Delesse, Deville, Cossa, and others have shown that mixtures of the silicates of alumina and the alkalies with over 70 per cent. of silica, must undergo a contraction to the extent of $\frac{1}{11}$th of their bulk in passing from a glassy to a highly crystalline state (granite). Mixtures of the silicates of alumina, magnesia, iron, lime, and the alkalies with less than 50 per cent. of silica, in passing from a vitreous state to a perfectly crystalline one (gabbro), must undergo a reduction in bulk equal to $\frac{1}{7}$.

It may fairly be anticipated, therefore, that great pressure would tend to promote the crystallisation of the mixtures of silicates composing most of the rocks of our globe, or to prevent their assuming the glassy state, and a great body of geological facts tends to support this conclusion. It must not of course be lost sight of that slow consolidation is also favourable to the process of crystallisation, and rocks being extremely bad conductors, the process of cooling in great rock-masses is excessively slow. It is often difficult therefore to discriminate between the effects that must be referred to slowness of cooling, and those which may be safely considered to result from pressure.

As long ago as 1846, Charles Darwin showed that the andesitic lavas of the Cordillera of South America are associated with perfectly crystalline rock, true granites, made up of precisely the same minerals. The identity of the minerals in the plutonic rocks and the lavas respectively was demonstrated by the careful studies of Darwin himself, and of Professor W. H. Miller, of Cambridge, long before the method of studying rocks in thin sections had been invented. Quite recently Professor A. Stelzner, employing the modern methods of research, has been able to completely confirm the interesting results arrived at by Darwin and Miller, and to show that a perfect gradation can be traced between the highly crystalline "Andengranites," and the more or less glassy lavas (andesites) which are so closely associated with them.

In 1874 I was able to show that in the Western Isles of Scotland there occur masses of perfectly crystalline (granitic) rock, identified by Zirkel as true gabbros and granites, which can be traced passing by the most insensible gradations into natural glasses ("tachylytes" and "obsidians") (*Quart. Journ. Geol, Soc.*, **30** (1874), 233—248), and the truth of these conclusions has been fully established by the more recent researches of Dr. A. Geikie (*Trans. Roy. Soc. Edinb.* (1888), 122—124, 145—150). In 1876 I further showed that the diorites and quartz-diorites of Hungary and Transylvania pass insensibly into the ordinary lavas of the district, which have the same ultimate chemical composition, and the same mineralogical constitution (*Quart. Journ. Geol. Soc.*, **32** (1876), 292). In 1885, Messrs. Arnold, Hague, and J. P. Iddings, of the United States Geological Survey, established precisely similar conclusions by the study of rocks in the Nevada district (*Bull. U.S. Geol. Surv.*, No, 17 (1885)); and Signor B. Lotti, of the Italian Geological Survey, in the following year proved the same to be true in the case of the rocks of Elba.

In all these cases it is seen that the masses which have been most deeply seated, and thus subjected to the greatest statical pressures, are those which have undergone the most perfect crystallisation. It must of course be remembered that in these cases the other cause tending to the development of crystalline structure comes into play, namely, slowness of cooling. The ordinary materials of igneous rocks are such bad conductors of heat, that enormous periods of time must elapse before the deeply seated portions of igneous rock-masses can become solidified.

The potent influence of this extreme slowness of cooling in bringing about the crystalline structure in molten masses of silicates has been well illustrated by the splendid researches on rock-synthesis by MM. Fouqué and A. Michel-Lévy. They have shown that the secret of making a particular mineral crystallise out of such a mass consists in finding out the temperature of fusion of the mineral, and in maintaining the molten mass for a long period just below this temperature. In the excessively slow cooling of deeply seated rock-masses, the materials must be kept successively and for long periods at temperatures a little below the fusion-points of each of their mineral constituents.

But while the influence of slow cooling in producing the crystalline structure in rocks is unquestionably very great, the effect of pressure in promoting crystallisation can scarcely be doubted. We have no proof, indeed, that the holocrystalline or perfectly granitic structure of rocks can ever be produced except under these conditions of extreme pressure.

II. *Crystallised minerals, developed in a magma under pressure, may lose their stability and be dissolved by the same magma, when the pressure is removed.*

The very remarkable researches of Fouqué and Michel-Lévy upon the synthesis of rocks is not less instructive, whether we consider the successes or the failures of their experiments. While able to reproduce by fusion and slow cooling—either from the powdered rocks themselves, or from duly admixed proportions of silica, alumina, iron oxide, and the alkaline earths and alkalies—various kinds of basalts and other basic rocks, all attempts to form certain other rocks, especially those containing quartz, hornblende, and muscovite, failed. The conclusion at which the experimenters arrive—and the correctness of these conclusions it is scarcely possible to doubt—is that, for the formation of such minerals and of the rocks containing them, water and other volatile substances, held within the solid mass by intense pressure, is absolutely indispensable.

Now in the porphyritic constituents (Einsprenlinge or phenocrysts) of many lavas, we find examples of minerals which have been formed at great depths in the earth's crust and then brought up to the surface and exposed to totally different conditions, especially as regards pressure. Very clearly do these phenocrysts tell the tale of their origin, and of the influence exerted upon them by their subsequent environments.

Crystals of quartz and felspar, which have grown to large proportions in the deeper portions of the earth's crust, are found when brought up in lavas to the earth's surface, and thus relieved from the action of pressure, to be attacked by the magma in which they were originally formed. The proof of this is seen in the corroded condition of the crystals, the glassy matter surrounding them having attacked their angles, their edges, and in a less degree their whole surface, penetrating irregularly into their interior, and reducing them sometimes to mere skeletons.

Crystals of hornblende and mica betray in an even more striking manner the effects of a change of environment. When brought up from great depths in masses of molten lava, crystals of these minerals are constantly found to be surrounded by "resorbtion halos." The outside of the hornblende or mica crystals, where in contact with the molten glass, is found to be attacked by it, and crystals of pyroxene and magnetite have resulted from the reaction. The action may in some cases continue till the whole of the hornblende has been converted into a pseudomorph.

In some instances there may be reason to believe that the phenocrysts have become enveloped in a magma of different chemical composition to that in which they were originally formed. But in many cases there is no room for doubt that the minerals which were formed and maintained their stability under certain conditions of pressure, lost that stability upon the diminution of pressure.

That, conversely, the increase of pressure leads to the production of a condition of instability in minerals formed at or near the earth's surface there cannot be any doubt. The study of the formation of crystalline schists from various aqueous and igneous rocks supplies us with numerous and very interesting illustrations of changes of this kind: hornblendes, chlorites, micas, and talc are produced under conditions of pressure in which pyroxenes, epidotes, felspars, and olivines lose their stability.

III. *In all those cases where solution is attended by contraction, the solvent action of water and other liquids is increased by pressure.*

That this is the case at elevated temperatures is proved by the researches of Daubrée to which we have already referred. Pure water was made to attack various silicates quite insoluble at ordinary temperatures and pressures. Even if we admit with Bunsen that there are temperatures at which this influence of pressure is no longer operative, or at which the effects are wholly inappreciable, the admission would not in any way affect the theoretical views of the geologist, seeing that the increase of temperature within the earth's crust is so rapid, that even at moderate depths the temperature at which solvent action is increased by pressure must certainly exist.

The *effects* of this solvent action under pressure are everywhere manifest when we come to the study of the rocks building up our earth's crust. At more or less considerable depths, water containing carbon dioxide has attacked the silicates composing the rock-forming minerals; so that it is impossible to find rocks which have been deep-seated, at any period of their history, in which the minerals are in a perfectly unchanged condition.

Great masses composed originally of calcic carbonate, are found to have been changed into dolomite (the magneso-calcic carbonate), or into chalybite (the ferrous carbonate); while in other cases the whole mass of a bed of calcic carbonate has been dissolved away, and silica substituted as a "pseudomorph."

We must proceed to study the details of such processes especially as they are affected by pressure and by the crystalline structure of the minerals affected.

IV. *Under great statical pressures, the whole substance of solid bodies may be permeated by fluids, and chemical reactions between them are thus greatly facilitated.*

It is not necessary to point out that the molecules of the densest solids cannot be in actual contact; this is proved by the circumstance that such solids undergo contraction by lowering of temperature, and that gases may be occluded in them. Physicists and mathematicians, as recently pointed out to this Society by Professor Rücker, have even been able to arrive at positive conclusions concerning, not only the actual order of magnitude of molecules, but the *distances* that separate them from one another in solids.

The effect of pressure in causing the molecules of one body to pass between those of another, has been expressed by Van der Waals in the dictum, "All bodies can mix with one another, when the pressure exceeds a certain value." A similar conclusion was expressed by the late Dr. Guthrie, as the result of his experiments on potassic nitrate, when he asserted that "fused nitre and fused ice are miscible in all proportions."

Now, nothing is more certain, from petrographical researches, than that the whole substance of the minerals in the deep-seated rock-masses of the globe may be permeated by fluids. This is shown by the condition of the minerals forming these deep-seated masses.

The felspars, in their normal condition, are colourless and transparent minerals with a vitreous lustre, and this is their character when they are found in lavas and in blocks ejected from volcanoes. In granites and other deep-seated rocks, however, these same felspars exhibit grey, green, pink, or red tints, with more or less opacity, and a remarkably pearly lustre. The cause of this change of aspect is found in the fact that the unstable alkaline silicates which enter into their composition have been attacked by the fluids that have penetrated through the whole substance of the crystal, leading to the formation of the hydrated silicate of alumina, and, in some cases, the peroxidation of any traces of iron compounds that may have been present in them.

Similar changes can be shown to have affected most, if not all, the minerals which, at any period of their history, have formed portions of deep-seated rock-masses.

V. *By the intimate intermixture, under great statical pressures, of solids and fluids, the properties of the former undergo great modifications.*

Bunsen, in common with all chemists who have studied the great problem of geology, has insisted that fused silicates, in spite of the high temperatures at which they assume the fluid state, obey the same laws as those governing ordinary solutions. Guthrie has shown that the principles which determine the formation of "cryohydrates" and of "eutectic compounds" are equally operative in the case of the separation of minerals from a mixture of fused silicates; and the same idea has been elaborated by Lagorio. Guthrie has further shown that as water is added to salt, the fusion-point of the mixture is progressively lowered, and from this fact he concludes that "the phenomenon of fusion is nothing more than an extreme case of liquefaction by solution."

That silicates, when they are mixed with water, fuse at a lower temperature, was long ago recognised by geologists—long, indeed, before any physical explanation had been offered of the fact. Poulett-Scrope, Scheerer, Elie de Beaumont, Daubrée, and many others who might be mentioned, have insisted on the important part played by water in promoting the fusion of lavas and other igneous masses.

In the case of the volcanic glass known as *marekanite*, I have shown that at a comparatively low temperature the mass will, when heated, swell up and intumesce, the escaping steam causing the molten glass to froth up and assume the character of a true pumice (*Geol. Mag.*, Dec. 3, 3, 243). The brown glass ejected from Krakatoa, during the great eruption of 1883, if heated, increases to many times its original bulk, and passes into a substance which, macroscopically and microscopically, is indistinguishable from the pumice thrown out in such vast quantities during that great eruption (*Geol. Mag.*, Dec. 3, 5, 6).

Many volcanic glasses contain an appreciable quantity of water, amounting in some cases, indeed, to as much as 10 per cent. of their mass. The glasses which contain water fuse at a lower temperature than those which are anhydrous. There is reason to believe that most lavas are not masses in a state of simple fusion, but consist of crystals floating in a mass of mixed silicates and water, the magma being at a temperature above the fusion-point of the mixture but below that of the crystals.

VI. *Mechanical stresses, which tend to overcome the attraction between the particles of a solid, promote chemical action at those parts of its mass which are in a condition of intense strain.*

That a direct relation exists between mechanical and chemical forces is shown by the fact that capillary action is capable of overcoming weak chemical affinities. Violent mechanical shocks will sometimes completely overmaster chemical affinity, as was shown by Berthelot in the case of acetylene, cyanogen, &c., and more recently by Professor Thorpe in the case of carbon bisulphide.

Carnelley and Schlerchmann endeavoured to show that the solution of a copper wire by acid was promoted when the wire was put into a condition of strain. These experiments, it is true, yielded negative results, a circumstance which is, perhaps, hardly to be wondered at, when we remember how feeble were the mechanical forces employed.

In the case of the curiously-impressed limestone pebbles of the Swiss Nagelflue, however, Sorby has shown that there are grounds for believing that solution is promoted in masses which are subjected to intense mechanical stresses, and he has confirmed this conclusion by an an ingenious experiment with rock-salt (*Yorksh. Proc. Geol. Soc.*, **4**, 458—461).

Similarly impressed and faulted pebbles from the Old Red Sandstone of Stonehaven, in Scotland, have afforded what I think is indisputable evidence of the action of strain in promoting solution. The sand-grains, of which these pebbles are composed, are seen under the microscope to be traversed by bands of liquid enclosures, that are clearly of *secondary* origin. Now, these bands of enclosures are parallel to the actual faults that have been produced in the pebbles, and the careful study of all the facts renders inevitable the conclusion that when the whole mass, under great statical pressures, was permeated by fluids, solvent action was determined in parts of the mass subjected to violent strain (*Mineralogical Magazine*, **7**, 83).

Similar bands of secondary liquid inclusions, which have clearly been produced in the same way, abound in the crystals of many rock-masses that have been subjected to strain and movement.

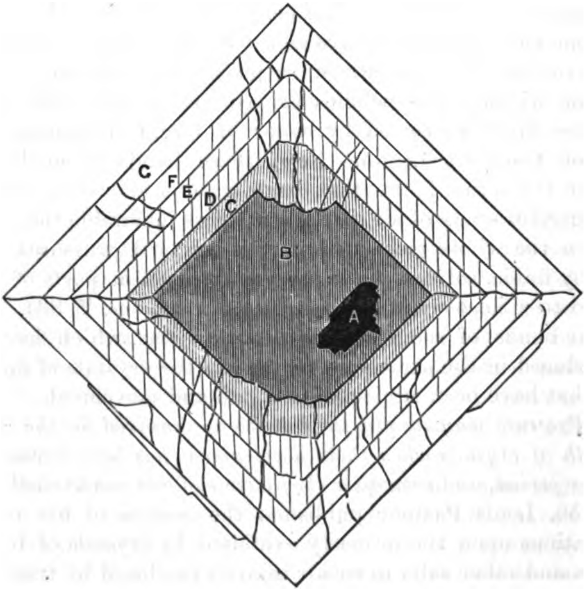
VII. *Pressure may supply the conditions required for the renewal of the growth of crystals when their development has been arrested for an indefinite period, and even after they have suffered mechanical injuries.*

In 1856, Louis Pasteur published the results of his interesting investigations upon the property exhibited by crystals of bimalate of ammonia and other salts to repair injuries produced by fracture; and this experiment has been repeated and confirmed by Scharff and other observers.

This principle of the growth and repair of injured crystals is one of great importance and wide application in geological investigation. Sorby has shown that rounded and water-worn sand-grains that have originally constituted a portion of a granite or other igneous rock may, in the presence of solutions of silica and under pressure, renew their growth, and, in the end, acquire the faces and angles characteristic of quartz-crystals. The observations of Becke, R. Irving, Van Hise, Bonney, and other microscopists have shown that, not only fragments of quartz, but portions of the crystals of felspar, augite, hornblende, biotite, and other minerals, may undergo enlargement in a similar way. It has further been shown that this repairing and growth of crystals is continually taking place in rocks under pressure; that the composition of the outer parts of a crystal may vary as growth goes on; and that the action can take place in solid rock-masses (*Quart. Journ. Geol. Soc.*, **45**, 175—186).

I have found it possible to illustrate experimentally some of the phenomena exhibited by zoned crystals in rocks. An octahedral crystal of chrome-alum of a dark-purple colour was mutilated by having two opposite solid angles broken off from it and then placed in a solution of common ammonia-alum (see Fig. 1). By more rapid growth in the injured portions, the crystal tended to repair itself, but the regularity of this process was interfered with by subjecting the crystal and solution to a somewhat wide range of temperature. As the coefficient of expansion of chrome-alum appears to be different from that of ammonia-alum, the shell of the latter material was from time to time cracked by the unequal expansion. The solvent, finding

FIG. 1.



its way into the interior, partially dissolved away the original crystal of chrome-alum. The final result of these changes was that while the form of the alum octahedron was almost completely reproduced, only a small portion (A) of the original chrome-alum crystal remained. Much of the chrome-alum was dissolved out and replaced by a mixture of the two alums (B), while the other layers of the crystal (C, D, E, F, G) were formed by still paler-coloured zones, also consisting of mixtures of a like kind. Zoned crystals exhibiting similar abnormal appearances to this alum crystal are by no means rare in some igneous rocks.

VIII. *When solution under pressure is going on in a crystalline body, the action is controlled and modified by its molecular structure. This molecular structure may have been produced either in the process of crystallisation, or as the result of mechanical or other forces acting upon the crystal subsequently to its formation.*

Daniell's earliest contributions to science, in the year 1816, dealt with the remarkable and unequal action of solvents upon crystals. The curious and complicated patterns produced on the faces and the cleavage or cut surfaces of crystals (etching-figures) have subsequently been studied by Leydolt, Klocke, Baumhauer, Becke, and other investigators. The results obtained have been shown to vary with the nature and strength of the solvent, the temperature, the pressure, and the time during which the action is allowed to take place.

In 1884–5 Von Ebner, as the result of an exhaustive study of the etching-figures of calcite and aragonite, showed that crystals possess *planes of chemical weakness*, to which he gave the name of "solution-planes;" these being analogous to the well-known planes of least cohesion or cleavage-planes. Quite independently, I, about the same time, arrived at the same conclusion by studying the crystals in deep-seated rocks (*Quart. Journ. Geol. Soc.*, **41**, 383, &c.). In these deep-seated rocks the crystals (their whole substance being permeated by the solvent) yield to chemical action along their solution-planes, along which hollow spaces in the form of negative crystals are produced.

When twinning-planes are developed in crystals by pressure or other mechanical agencies, these planes (gliding-planes) become planes of chemical weakness (*Mineralog. Mag.*, **7**, 87). The experiments of Reusch, Baumhauer, Mügge, Foerstner, and others have shown how frequently this secondary twinning is developed in the crystals of rock-forming minerals.

When the negative crystals formed along the solution-planes of a mineral are filled with various secondary products, the whole character and aspect of the substance may be transformed. When the infilled negative crystals are of appreciable dimensions, the avanturine and "schiller" phenomena result from the action. When the action is on an ultra-microscopical scale, the phenomena of opalescence and of iridescence may be produced.

By the introduction of various substances in solution into a crystal, its composition may be altered and the way prepared for the recrystallisation of the substance as a distinct mineral. It has been shown that by the introduction of sodic chloride into a plagioclase-felspar, the way has been prepared for the conversion of that mineral into scapolite (*Mineralog. Mag.*, 8, 186).

IX. *Under great pressures, paramorphic changes take place in crystalline bodies, without any alteration in their chemical composition.*

It is a well-known fact that, under the slight pressure which can be exerted by the hand, the orthorhombic, yellow variety of mercuric iodide passes into the tetragonal, red variety. Spring has shown that, under a pressure of 5000 atmospheres, monoclinic sulphur passes, at ordinary temperatures, into the orthorhombic form. Van't Hoff and Reicher have shown that the temperature at which this latter change takes place is progressively diminished as the pressure is increased.

That slight forces acting through a considerable period of time are competent to produce such paramorphic changes has long been known. Thus the mercuric iodide and sulphur undergo their paramorphic changes slowly, when subjected only to the ordinary vicissitudes of atmospheric temperature.

Many interesting examples of similar heteromorphous forms of the same compound are familiar to geologists: such as calcite and aragonite among the carbonates, and pyroxenes and amphiboles among the silicates. Heteromorphism, indeed, appears to be the rule rather than the exception in the mineral kingdom.

The slow paramorphic changes between heteromorphous forms of the same compound was long ago studied by Gustav Rose; and in more recent years the dependence of these changes on great pressures, or on small forces acting through long periods of time, has engaged the attention of J. A. Phillips, Allport, Hawes, R. D. Irving, J. Lehmann, G. H. Williams, Teall, and other observers.

In considering these paramorphic changes, it must be remembered that the transition under pressure is not always, as in the case of sulphur, from a less dense to a more dense form. On the contrary, as in the change of both aragonite to calcite, and of augite to hornblende, we find the denser but less stable form passing into the less dense but more stable one. Stability, however, is only a relative term: while one form of a compound may be most stable at one temperature or under a certain pressure, other conditions may exist under which it becomes an unstable form.

X. *Both solution and the formation of new crystalline compounds may result from pressure, and these two operations may take place together; in this way more or less complete interchange of ingredients may take place between the crystalline bodies, and pseudomorphs be formed.*

That most of the pseudomorphic changes, so common in the mineral kingdom, take place at considerable depths from the surface, there seems no room to doubt; and in all these cases it may be inferred that pressure is one of the determining conditions of the action.

The effects of these pseudomorphic changes in transforming vast rock-masses into others of totally different composition—such as limestone into dolomite, chalybite, or silica—has long been familiar to geologists; and modern microscopical methods have enabled us to trace the progress of these changes from their earliest beginnings to their complete consummation.

Without entering further into this very wide question, I may mention that Mr. G. F. Becker has lately published the full details of his studies of the Coast-Ranges of California, and that these tend to prove that, in comparatively recent geological times, vast masses of rock in that district have had their substance replaced in some cases by silica, and in others by serpentine; the changes sometimes taking place over considerable areas. These conclusions, arrived at by the officers of the U.S. Geological Survey, if fully established—and there appears to be no room for doubt as to their general accuracy—are not less interesting and suggestive than they are novel and startling.

XI. *When, as the result of dynamical pressures, the crystalline constituents of rocks are brought into close contact, chemical affinity comes into play between them, and new mineral species result from the reactions that take place. This operation is facilitated, when, as a consequence of internal strains, differential movements are set up within the rock-mass, and rubbing or sliding contacts between its particles are brought about.*

Chemists are acquainted with many examples of chemical action following from the simple bringing into close contact of molecules. In the union of gases, when they are condensed by platinum-black, and even in the light rubbing of a safety match on the match-box, we have illustrations of such phenomena

Spring has shown that, when powdered metals are mixed together and subjected to great pressures, union takes place between them, and alloys are formed. When dry anhydrous salts are similarly treated, double decomposition takes place, and new compounds are formed.

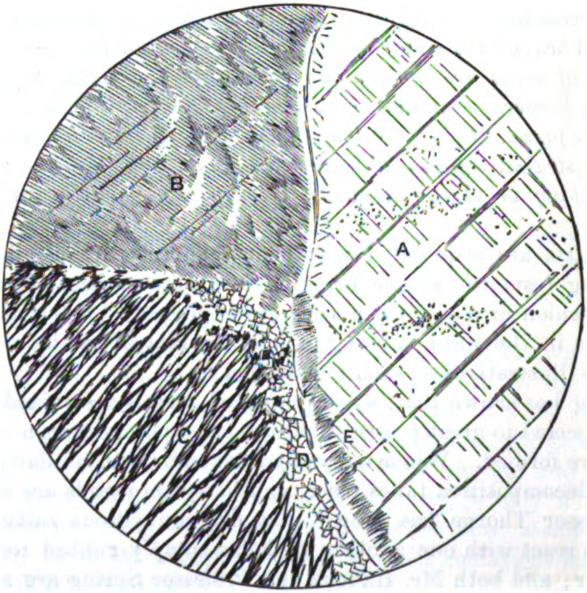
Professor Thorpe has shown that dry, anhydrous salts may be made to react with one another by being simply rubbed together in a mortar; and both Mr. Hallock and Professor Spring are agreed as to the intensification of action which occurs when rubbing or sliding movements—attended with necessary multiplication of points of contact in compressed bodies—takes place.

Lastly, it may be pointed out that Spring has recently shown *time* to be a very important factor in such changes, by allowing slow diffusion to take place at the surfaces of contact.

That the rocks known as "crystalline schists and gneisses" have had their peculiar characters produced by "internal differential movements," resulting from "enormous irregular pressures," was clearly recognised by Poulett-Scrope, Darwin, Naumann, and Sharpe, long before the researches of physicists and chemists had supplied us with the explanation of the phenomena. Modern petrography has confirmed and illustrated these conclusions, enabling us to study the actual stages of the processes of change by which, through the reaction of the constituent minerals of a rock under pressure, the whole mass resolves itself into a completely different mineral-aggregate. The labours of Lossen in the Hartz, of J. Lehmann in Saxony, and of H. Reusch in Norway have been of especial value in establishing these important conclusions.

As an illustration of this kind of action, we cannot, perhaps, do better than take the case of a rock (gabbro) consisting of three somewhat unstable constituents (see Fig. 2), labradorite (A),

FIG. 2.



pyroxene (B), and olivine (C). In the rock from which the figure has been taken, there are clear evidences of its having been subjected to deforming stresses. Where the olivine, the least stable of the three minerals, is in contact with the labradorite, the silicates of which they are composed have reacted upon one another. The result is seen in the formation of a zone between them consisting of entirely new minerals, a pyroxene (D), and a hornblende (E). Similar changes, but not so strongly marked, are seen to be in progress between the olivine and the pyroxene, and between the pyroxene and the labradorite.

By carefully selecting and studying a series of specimens from the same rock-mass, every step in the metamorphosis of a rock may be followed, from incipient changes like those in the case above illustrated, to the final disappearance of every vestige of the original mineral constituents of the rock, and the substitution of new mineral species.

XII. *When internal strains and differential movements affect a mass, which is at the same time undergoing recrystallisation, the forms and relations of the crystalline particles that build up the new rock may be greatly modified by the action of the mechanical forces.*

That perfect rest is a condition upon which well-developed crystallisation depends, is a fact too well known to need dwelling upon here. That very small mechanical causes, such as the presence of foreign bodies, or the existence of rough surfaces, may determine the size and position of crystals in a solidifying mass, is also a fact familiar to every chemist. By stirring or similar movements carried on within a crystallising mass, granulation, or the formation of a number of small imperfect crystals, rather than of large and well-developed ones, is brought about; as in the well-known Pattinson's process for desilverising lead.

The evidence of perfectly similar actions having taken place in crystallising rock-masses is everywhere conspicuous; and the results are the same, whether the crystallisation occurred in a mass passing from a fluid to a solid state, or in a mass which remained solid during the whole process of recrystallisation.

There are two structures which are especially exhibited by rocks that have been subjected to dynamo-metamorphism which seem clearly to have been produced by such causes; these are the structures known as the *granulitic* and the *foliated.*

The *granulitic* structure, which is so well exhibited by the rocks called "granulites," is characterised by the crystals assuming the form of granules, having more or less rounded outlines, and lying in every position; so that, under the polariscope, the mass resembles a fine mosaic. I have shown that well crystalline rock-masses (gabbros), when forced in a molten state through great fissures, assume on their edges, where much friction must have occurred, this granulitic habit, which is sometimes exhibited in a very striking manner (*Quart. Journ. Geol. Soc.*, **42**, 76, &c.).

The foliated structure, so characteristic of schists and gneisses, consists in the separation along nearly parallel planes of leaf-like patches (folia) of the several mineral constituents of the crystallising mass. Poulett-Scrope, from his study of the viscous lavas of Ponza, Lipari, and Hungary, and Darwin, from his study of the similar lavas of Ascension, were able to show that these rocks, under similar conditions, often assume a *foliated* structure. Perfectly granitic rock-masses, like the syenite of the Plauenschen Grund and the granitite of Aberdeen, sometimes exhibit on their margins a distinctly foliated structure.

It is worthy of notice that both the granulated and the foliated structures are produced in recrystallising masses that are subjected to internal strains and differential movements. They are equally produced when the mass has been a liquid which has slowly passed into the solid state by the process of crystallisation; and when by the processes we have already considered the mass, *retaining its solidity*, has undergone internal molecular rearrangement and recrystallisation.

A rock-mass behaves as a viscous body, under slight pressures, when heat and the presence of water have overcome the cohesion of its particles. But the researches of Tresca and Daubrée have shown that, when subjected to sufficiently powerful stresses, the most perfectly solid bodies we know of behave like viscous bodies, and can be made to *flow*.

In the foregoing remarks, my main object has been to show how far the physical and chemical principles, which have been established by actual experiment, are capable of explaining the phenomena observed by the geologist in studying the earth's crust. I have especially avoided invoking any causes which must be regarded as hypothetical.

Some of the actions relied upon as explaining the origin of the great features of the rock-masses which compose the earth's crust may seem at first sight small and even insignificant. But the great lesson taught by modern geological science is that such small forces, operating upon enormous masses of matter during vast periods of time, are capable of effecting the most stupendous results.

In speaking of *statical* pressure, I have not treated it as an agent of change, like heat or electricity, but simply as a condition under which these agents operate—one which may profoundly modify or control their action. Such pressure, too, may produce great effects by causing a closer contact and consequent chemical action between the molecules of a fluid made to penetrate a solid, or between the molecules of two solids forced into more perfect contact. Statical pressure may, further, prevent the escape of volatile materials even under extreme temperatures, and these substances, as in the case of the "mineralisers" of the French chemists, may exercise important influences on the solids or liquids within which they are retained.

Dynamical pressure, especially when it results in differential movements in a mass, can certainly do all that is effected by statical pressure, and perhaps something more. That such motion is converted into heat there can be no doubt; and some geologists, like the late R. Mallet and Professor Prestwich, have argued that the heat so produced must have played an important part in the work of metamorphism. But considering the slowness with which the earth-movements have probably taken place, and the opportunities for the dissipation of this thermal energy, it may be regarded as at least doubtful if at a particular point in the rock-mass the temperature could ever have been raised to such an extent, that any very important part of the work of metamorphism ought to be ascribed to it. In the same way, we may, perhaps, regard the suggestion of Mr. Sorby that, during great earth-movements, mechanical energy is directly converted into chemical energy, as one in favour of which no convincing evidence has as yet been adduced.

It is at least conceivable that the realm of excessively *high* pressures is one in which phenomena may be displayed which are as anomalous as those exhibited under extremely *low* pressures—the high vacua of Mr. Crookes. But until such effects have been demonstrated by actual experiment, it is unwise to invoke their aid in geological hypothesis. My great object, in the remarks I have ventured to offer you this evening, has been to show that on well-established physical and chemical principles, the phenomena, which are exhibited by rock-masses that have been subjected to great pressures, are capable of satisfactory explanation.

ANNUAL GENERAL MEETING,

March 27th, 1890.

Dr. W. J. Russell, F.R.S., President, in the Chair.

The Report I have the honour to lay before you to-day shows that our Society continues in a prosperous condition, and even, if we look back to the time of its foundation, now nearly half a century, we see how remarkably continuous and uniform the increase of the Society has always been.

The following tabular statement gives the numerical position of the Society:—

Number of Fellows (March 21st, 1889)		1614
Since elected and paid admission fees		145
		1759
Removed on account of arrears	34	
Withdrawn	12	
Deceased	15	
		61
Present number of Fellows		1698
Number of Foreign Members, March 31st, 1889	36	
Deceased (M. Chevreul, Dr. A. Geuther, and Professor Lœwig)	3	
Present number of Foreign Members	33	

I may epitomise it by saying that this time last year there were 1614 Fellows; there are now 1698, an absolute increase of 84, which is above the average number. There have been 145 elected, but 34 have ceased to be Fellows on account of non-payment of subscriptions, 12 withdrawn, and we have lost 15 by death.

Of the 36 foreign members this time last year we have lost three (Chevreul, Geuther, and C. Lœwig) by death.

The deceased Fellows are:—Richard Anderson, M. T. Buchanan, John Dale, Warren de la Rue, Ernest H. Francis, James Hindle, J. P. Joule, Benjamin Nickels, David Page, Henry Pollock, Owen

Prosser, R. Romanis, Edmund Ronalds, Joseph Stapleton, and David Waldie.

Withdrawn:—S. F. Burford, E. B. Clarke, N. M. Falkiner, Alexander Galt, John Innes, Alfred Neild, Walter F. Pankhurst, Forbes Rickard, Newton Samuelson, S. D. Titmas, W. Weston, G. H. With, and Charles Williams.

The financial state of the Society is, as you will presently hear from the Treasurer, very satisfactory.

The sum of £236 16*s*. 1*d*. has been, during the year, expended on the purchase of books and periodicals, and a further sum of £37 10*s*. on additional book shelves. The following table shows the numerical strength of our Library as compared with last year:—

	March 31st, 1889.	Additions in 1889–90.	Present State.
Volumes of systematic works..........	2,922	160	3,082
Volumes of journals..................	5,474	193	5,667
Volumes of duplicate journals for circulation	1,084	51	1,135
Pamphlets..........................	1,426	24	1,450
	10,906	428	11,334

For the judicious increase to our Library, the Society is much indebted to the Library Committee, who are most energetic and prompt in their action, selecting, I believe, with much judgment, the books which should be added to our shelves, and declining a still larger number, which, from their character, or only slight relation to chemical science, are not worthy of a place in our Library.

In addition to the very considerable number of new books added during the year, I would note that a very important addition of older works on chemistry has been made, partly by purchase, but to a very considerable extent by the generosity of some of our Fellows and others. Books of this kind, it is well known, are becoming every day more difficult to obtain, and your Committee lose no favourable opportunity of securing such volumes as are really illustrative of the development of our Science; still, for the Society to possess a really complete collection of historical works on chemistry—and this is certainly an object of much importance—we must, to a considerable extent, appeal to the generosity of our Fellows; and I would remind them how much the value and interest of an old book are increased when it becomes the integral part of a series of historical works, such as our Society already possesses.

At the present time our Library is, I believe, more complete, with respect to chemical works, than any other library with which it can be fairly compared: but this is not sufficient; it must be a library which possesses not only all modern chemical books of real value to the investigator, and to the student, but, in addition to this, it must contain all books required to trace, even in detail, the growth and development of chemical science.

There is still another numerical statement which it is my duty to lay before you: it is with regard to the number of communications which have been made to the Society during the year. Last year 75 original papers were published in our Transactions, this year, that is, since the last anniversary meeting, 72. The papers last year occupied in our annual volume 895 pages, this year 772 pages. The total number of papers communicated to the Society, all of which appeared either in full or in abstract in the Proceedings, is 100, and this number is 3 less than last year. The number of abstracts of papers published this year is considerably less than last year, when it was exceptionally large; the number this year is 2131, last year it was 2470; this year they occupy 1252 pages, last year 1351 pages; thus our Journal is somewhat smaller this year than last, but as compared with former years retains its usual size, and, I certainly may add, its high character.

The Publication Committee spare neither time nor labour to make the Journal as perfect as possible, and their efforts are well seconded by our able Editors. The literature of our science now grows so rapidly, that even our 2000 abstracts are not sufficient to do full justice to it, the number will have to be increased, and we intend that this increase shall include a more complete and detailed account of the analytical side of our science.

I cannot leave the subject of our publications without calling your attention to the Proceedings, as they are now shortly named. They have now existed for nearly six years, and are a most valuable adjunct to our Journal, serving to give as wide and as important a publicity to a paper as the Transactions, and at the same time to afford a rapidity of publication not exceeded by that of any scientific journal. I think I may add that no Society can boast of publications more complete, thoroughly useful, and up to date, than ours.

In the volumes of our Journal we have a tolerably complete account of the contributions made by British chemists during the last half century to scientific chemistry, and I think that anyone, on glancing through these volumes, will be struck with the large amount of thoughtful and accurate work there recorded, work which is still of high value to the original investigator and to the student.

The increasing difficulty of ascertaining what has already been accomplished on any subject,' the loss of time arising from doing what has already been done, is felt by all workers, and I should, therefore, like to mention to you a proposition which has been made, namely, that the most fitting memorial which the Society could institute of its Jubilee, which occurs next year, would be the preparation of a complete subject catalogue of its Journal from its commencement. That such a work is practicable, and that the Society has the means for carrying it out, there is no doubt, and I cannot but think that to render easy of access the large store of information contained in our Journal would repay even the great labour and expense of so serious an undertaking.

In his address last year the President had the pleasure of announcing that the Davy Medal of the Royal Society had both that year and in the preceding year been awarded to Fellows of our Society, and I am sure we all heartily confirmed the choice of Mr. Newlands and Mr. Crookes as worthy recipients of this high honour. I am happy to be able to-day to state that this year still greater honour has fallen to our Society, for not only has a Davy Medal, but also a Royal Medal, been awarded to Fellows of our Society, and I am sure we all rejoice that the important investigations of Dr. Perkin and of our Treasurer, Professor Thorpe, have met with so well deserved a recognition of their value.

There are still some matters intimately connected with the working of the Society which call for remark on this occasion; one is the change which now, for the first time, occurs with regard to our meeting to-day. The anniversary meeting has, I believe, hitherto always been an evening meeting, and I am sure all who heard, and all who have since read, the address which my predecessor then gave, recounting the achievements of the spectroscope in the difficult investigation of the rare earths, will remember how he converted a prosaic business meeting into one of more than ordinary scientific interest; but the Council, while far from desiring to discourage such communications, considered that it would be of advantage to the Society in general to follow the example of other societies, and, on the anniversary, have two meetings, one in the afternoon for the transaction of the Society's business, and hearing the annual report, and the other of a social character, at which the Fellows and their friends would dine together. This alteration will, doubtless, tend to bring a large number of our Fellows together, and we hope that many of those not resident in London will feel it to be a duty, as well as a pleasure, to attend at least the annual evening meeting of the Society.

The admirable lecture which we heard at our last meeting, from Professor Judd, will be fresh in your minds, and I am sure the Society feels how much it is indebted to him for his discourse. It is as far back as 1854 that the Council first established the occasional delivery of lectures in place of the reading of papers, in order, as the minute states, to give additional interest to the meetings of the Society. An important change has gradually occurred with regard to the subjects for these lectures. At first they were of a purely chemical character, and the lectures were given only by Fellows of our Society; now the subjects chosen belong rather to the border-land of our science than to pure chemistry; and the lecturers of late have not been Fellows of our Society. The strikingly important and interesting discourses which we have of late had, in one case from a physicist, and in another from a geologist, well illustrate the great importance at the present day of an intimate communication among those who are working at different branches of science.

One other matter connected with the working of the Society I must mention, and that is the proposal to hold an extra meeting on the 8th May next, to be devoted to the exhibition of new forms of apparatus. In all active laboratories there is to be found apparatus which, from time to time, has been devised generally to meet some special requirement; and, although it may completely have answered its purpose, still the inventor does not consider it worthy of record, and it is never known beyond the laboratory where it was invented. Probably still more numerous are the modifications of older forms of apparatus which never become known; it is, therefore, hoped that much information of a very substantial value will be disseminated by our devoting an evening to the exhibition and examination of apparatus such as I have described.

I do not propose to-day, taking as my text the number of original papers communicated to the Society, discussing, as so many of my predecessors have done, the position of original research in this country; but I do desire to make some remarks—and they shall be brief—on another subject, and one which is not of less importance, both to this country and to this Society: it is that of teaching chemistry; the subject is a wide one, but my remarks will be directed, so far as it is possible, to only one phase of it—that of teaching chemistry to the students of medicine. I do not know that anyone would advocate the present system of instruction as perfectly satisfactory, but there are some, I believe, who would advocate the omission of chemistry altogether from the education of the medical student, and certainly would affirm that it is of little, if any, use to the ordinary medical practitioner, supporting this view by the fact that both medicine and surgery are successfully practised by those who have no chemical knowledge. The value of this opinion I will not stop to discuss here, but would simply note the fact in passing; for it does not seem always to be acknowledged that the fundamental action of medicines, the origin of their power, is a chemical change, and, hidden and complicated as these changes may be, they must ever retain their chemical character. That an empirical knowledge of the results of such changes can, in many cases, be gained by continued experiment is true, but if an understanding and appreciation of results is to be sought for, then the first step must be to learn the chemical nature of the bodies employed, and the laws which govern chemical action.

Chemistry has, however, another claim for being studied, in addition to its furnishing so many of the elementary facts on which medicine rests: it is that a better schooling could not be devised for the student of medicine than a study of these facts in their simplest form. Chemistry has now become so far an exact science, and the phenomena with which it deals so easily lend themselves to repetition and confirmation, that it is capable of being taught in a way which, as a mental exercise, is of the highest value; and in the case of the student of medicine this mental training can be combined with the acquirement of knowledge which in itself is directly useful, not to say absolutely necessary, for him to possess.

Attention has lately been drawn to the teaching of chemistry, especially in schools, by the Reports of the British Association Committee on this subject, and it is difficult to over-estimate the importance of encouraging good school teaching, for not only does school teaching exercise an important influence on the extent of knowledge of the science, but also on the appreciation of it. Impress schoolboys, by bad teaching, that chemistry is not worth learning, and you have given them an impression which the majority will never get over; and the reverse is true: an intelligent teaching of the elements of the science leads to a study, in after life, of the higher branches of the subject. The teaching of chemistry, as a part of school education, is of late date, and, even now, is restricted very much to the larger and more advanced modern schools.

In the first Report of the Committee before alluded to, it is stated that of the schools which answered a circular requesting information as to their science teaching, and which represented some 23,350 pupils, only 36 per cent. of these received chemical instruction; add to these all the other pupils at schools from which no reply was received, and at which probably little or no chemistry was taught, and the total number learning chemistry must be far below 36 per cent.; there is, however, every reason to believe that the number, small though it be at present, is rapidly increasing. In addition to this school-teaching, it is not, I think, generally known how large an amount of chemical instruction is stimulated and directed by the Science and Art Department. At the present time the students in these chemical classes must number very nearly, if not quite, 30,000, and it will give some idea of the activity of these classes when I say that at the last annual examination the students sent in 25,400 examination papers, and that the elementary classes in practical chemistry required no less an amount of solid substances for analysis than 2½ cwt.

That this systematic teaching of chemistry, so widely diffused over the whole country and so largely increasing every year, exercises a very important and very beneficial influence is beyond doubt.

At a previous Anniversary Meeting, my predecessor pointed out how detrimental to the study of chemistry in schools would be the adoption of the new scheme of marks proposed for certain entrance examinations at Sandhurst and at Woolwich, for while as many as 3000 marks could be obtained for mathematics, either compulsory or optional, and also for Latin, French, and German, only 2000 could be obtained for chemistry, thus rendering it a second class optional subject, and giving it a position which would induce very few, if any, boys to study it. I am happy to say that this scheme has been revised, and that chemistry now takes a far better position, for it will now be on a level, as far as marks are concerned, with the other subjects, excepting mathematics. It still, however, remains only an optional subject, while Latin, French, or German are compulsory ones. It is, I believe, to one of our Fellows, Sir H. Roscoe, that we are principally indebted for this change of scheme, which is one of no small importance.

Another question with regard to the school teaching of chemistry, and one of even greater importance than that of the number taught, is, how is it taught; is the character of the teaching the best that can be devised? On this point we must bear in mind what I alluded to just now, the very recent introduction of chemistry as a school subject; it could hardly be expected that teachers, even if they had been allowed a free hand, and could have carried out the systems they believe to be best, would, without experience, have adopted the most perfect methods of instruction; but the free hand undoubtedly has not been allowed to them, and they have been weighted by a want of means, a want of time, and in some cases a want of knowledge; consequently much of the instruction has been of a character far from perfect: it neither encouraged accuracy of thought, power of observation and deduction, nor did it add to the pupil's knowledge of what was likely to be of use or interest to him. That chemistry can be taught to boys so that it is a mental training certainly not inferior, I think I may say superior, to any other subject on his list of studies, is now admitted by many who have considered fully this question, and all allow that the facts of the science can be presented to young students in a way that not only opens out to many a new and unsuspected world, but gives to all information that is of use and interest.

I must again refer to the Reports of the British Association Committee, in order to call your attention to a scheme which that Committee have endorsed, but which has been drawn up by Professor Armstrong, indicating the line and the spirit which should be adopted in elementary teaching. I believe that chemical teaching in the future will be of the kind and character here indicated, and if this scheme leads, as it must do, to a more thoughtful, accurate, and logical way of teaching chemistry, it will accomplish a most important work, and will, without doubt, largely increase the number of persons who sympathise with the objects of our Society. I have dwelt on this part of the subject because I want you to feel that even if the school teaching has been imperfect, attention is now drawn to it, and we may be confident that, as each year passes, not only will the number of students of our science increase, but that the quality of the teaching will improve, and this is essential to the suggestions I am about to make with respect to the students of medicine.

The schoolboy becomes the medical student, and once entered on this line of study, the work before him is large, and appears to be increasing. Among the multitude of subjects for study forced upon the student, is it necessary that chemistry should be one? May it not be a subject from which the ordinary practitioner can be relieved, and be reserved only for those who are studying the higher branches of the profession? The answer, I think, is, clearly and emphatically, "No." A knowledge of the nature of the agents with which he is to deal, a knowledge of the laws by which their changes are ever regulated, must in all cases form the real basis on which his after-acquired learning is to rest. I value, also, as most precious to the student, the opportunity which the study of chemistry affords him of learning how accurate knowledge is obtained from experiment, and how investigations, if they are to lead to useful results, must be carried on.

That a wide knowledge of the science is necessary for the student I do not think is the case; his knowledge should be a knowledge of elementary principles, but principles learnt in such a way that he has grasped their real meaning and can apply them to new cases.

Chemists in the past have, I think, unduly urged an extensive knowledge of their science as necessary—have, in fact, been inclined to consider that every medical man should be a fully educated and experienced chemist.

There is no doubt the knowledge which this implies would be most useful, and, no doubt, he would have many opportunities of using such knowledge, both for his own advantage and also for the extension of science; but, after all, the time for study is but short, and the problem really is, what is it most important the student should learn?

For my own part, I willingly relinquish the idea of making him a chemist, but most pertinaciously do I adhere to the statement that he must be well trained in elementary chemistry. The importance of starting on right lines and on right principles applies with much force to the student; encourage him to look upon elementary knowledge as of no use, on the methods by which knowledge is gained from experiment as of no avail to him, and you are educating men to become empiricists, not fitting them to become observant and reasoning human beings.

You will bear in mind I am speaking of what is the smallest amount of chemical knowledge which should be considered sufficient for the ordinary student of medicine. A student who desires a wider knowledge of physiology must extend his knowledge of chemistry—the two cannot be parted; but the commencement of the study would be the same for all, and I believe it should be made at school or before the student enters a medical college; in fact, I think that chemistry should be placed in the same category as the subjects of general education and made an obligatory subject in the preliminary examination. It would be necessary clearly to define the extent and character of the teaching required for preparing candidates for such an examination, and I am convinced that all our leading schools would gladly undertake such teaching, and I think would profit by the definite task thus set before them. One point with regard to this teaching is of much importance: it is that it must not be in any way technical; it must, as far as possible, deal with simple elementary principles, and not be a cramming of the pupil with useful practical facts.

The testing of the candidate's knowledge must be a reality, not a fiction; it must be done with thought and judgment, partly by written papers and partly by interrogation; no restriction I fear as to how or when the knowledge had been gained could be enforced; the examination alone must determine whether the knowledge in extent and character is up to the required standard. In this way it would be insured that all students on commencing their medical studies would have some knowledge of chemistry, and then the teacher at the medical schools would commence his instruction at a higher level than at present; he might assume that his students were familiar with the rudiments of the science, were familiar with the terms employed, and had some idea of how knowledge was derived from experiment. Even under these more favourable conditions the extent of chemistry to be taught should, compared to the whole science, be but small; the elementary principles which had before been indicated would now be extended, enforced, and more fully illustrated, the illustrations being drawn by preference from changes with which the student is or will be most familiar; in this sense the teaching would have a technical bias. With regard to the extent to which this chemical teaching should be carried, the conjoint Board of the two Colleges have, I believe, at the present moment, a carefully considered syllabus under consideration indicating the range of chemical knowledge to be required from all students of medicine.

Among the many very efficient regulations drawn up by the examining Board of the two Colleges there is one against which I wish to protest. In all cases except chemistry the Board insists that the subject, be it physiology, anatomy, or medicine, shall have been studied at a recognised medical school, thus, as it seems to me, most wisely insisting on the fact that every student presenting himself for examination shall have carried on his studies under efficient instructors and at places properly equipped for the work they undertake. I think that this same restriction should apply to chemistry. At the present time the candidate, on presenting himself for examination, has only to produce a certificate stating that he has received chemical instruction; if only qualified persons gave certificates they would be of value; as it is, I fail to see the use of these certificates. Further, it is obvious that, if examinations were perfect and showed exactly the mental condition of the candidates, all limitations as to place of study would be unnecessary; but at the present time a strong feeling is growing up that a most valuable, I might almost say necessary, adjunct to all examinations is a knowledge of where the student has studied, and a guarantee that he not only has had proper and sufficient opportunities for study, but also that he has made proper use of such opportunities. To waive all such restrictions in the case of chemistry does not seem to me to be right; I believe the restriction is very beneficial, as applied to the other subjects of medical education, and that a theoretical and practical subject such as chemistry would also be better learnt if certain restrictions were imposed; at the same time, I do not advocate that a monopoly should again be granted to medical schools, and only students who have learnt chemistry at these institutions be eligible for examination, but I would oblige every candidate to produce a satisfactory certificate from an efficient and properly equipped school of chemistry. If this cannot be done, then it only remains for everything to depend on the examination; it must be far more searching than at present, and in place of lasting for hours it must last for days.

I am convinced that it would be of great advantage to the student that his study of chemistry should occur at two distinct intervals. At present, with many students, the commencement and the end of his chemical studies are embraced within a few months, and the subject so learnt is forgotten within a still shorter period. The more gradual absorption, and more leisurely assimilation, of the subject is required. In addition to the chemical teaching already indicated, in every medical school there should be a higher class for students who have time and inclination for a more thorough education; even in such a class the subject must still be treated as a science, becoming however somewhat more technical in character, and it should be set before the student in such a way as to enable him clearly to see its application to the other subjects he is studying. To a far greater extent than is the case at present, I think the teacher of physiology and the teacher of chemistry should work together; now the student looks upon the chemistry of the chemical teacher as something distinct and not nearly so necessary as the chemistry of the physiologist; a more intimate connection between the two would give additional interest and importance to the teaching of both. In the foregoing remarks I have attempted to sketch in brief outline what I think should be the course of chemical instruction for medical students, and I have limited my suggestions to such alterations as I believe to be even at the present time practicable. The perfecting of this or any other scheme can only be done satisfactorily by those who are actively engaged in teaching, and who understand what the aims of education are, freely discussing the subject. Medical teachers have looked upon the chemist as an outsider, not to say an intruder, and alarmed by the demands which the chemist has made on the student's time, have endeavoured to exclude, as far as they could, all chemical teaching. At the present time I think a more rational feeling is springing up on both sides; each is acknowledging the importance of the other's teaching. No cultivator or teacher of any branch of science can now stand alone; the connection and diffusion of one science into others is one of the most marked features of the time, and the border-lands of many sciences which but a few years ago were unexplored and uncared for have now become ground of great value and importance. I would even admit that formerly, when the prescribed time for study was less than at present, the chemist may have asked for more than his due share of it—not that the student ever acceded to this demand—and further that the teaching was not always well adapted to the requirements of the case. The science had then, as it has now, difficulties in its teaching: formerly, when of much smaller extent, the student listened to a categorical account of nearly all the well-known compounds of well-established elements, and the lecturer was glad if his knowledge supplied him with a sufficient number of facts to fill his lectures from October till April; now the difficulty is of an opposite kind—the lecturer is overwhelmed with the abundance of material, and this demands from him a great amount of thought and judgment to enable him to select the materials which best illustrate the most important elements of his science. The day for lectures to be a mere recital of facts is past; the facts are always to be found in text-books. Now the lecturer must give a living account of the principles of his science, grouping and marshalling his facts so as to show how general conclusions are arrived at. That most important adjunct to lectures on chemistry, experiment, if it is really to serve its purpose, requires not less thought and judgment than the subject-matter itself. The text-book must supplement the teaching of the lecturer, but at the present time efficient aid of this kind is not supplied to the student of medicine. It is members of our Society who can best realise the advantages to be derived from a careful and accurate study of chemistry; it devolves then upon them, while not blind to the importance of other studies, to advocate chemistry taking its proper place, and being properly taught not only to the medical student, but, as a branch of general education, to all other students.

Sir F. A. Abel proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed; Professor Emerson Reynolds seconded the motion; Mr. Cassall also spoke on behalf of the motion, which was carried by acclamation. The President having acknowledged the vote,

Professor Thorpe, the Treasurer, gave an account of the financial position of the Society. The receipts by admission fees and subscriptions had been £3637; by sale of the Journal £377 3*s.*; and by dividends on invested capital £340 10*s.* 9*d.* The expenses on account of the Journal had been £2310 18*s.* 3*d.*; on account of the Proceedings, £177 4*s.* 7*d.*; on account of the Library, £420 8*s.* 11*d.*: the total expenditure being £3578 18*s.* 8*d.* £530 had been invested in Metropolitan Board of Works 3½ per cent. stock, and the balance in hand was £2036 2*s.* 7*d.*, as against £1833 13*s.* 6*d.* at the corresponding period last year.

Dr. H. Müller proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; the motion was seconded by Professor Dunstan. Professor Thorpe, after replying, proposed a vote of thanks to the Auditors, Messrs. R. H. Davies, Bernard Dyer and R. J. Friswell; this was seconded by Mr. F. J. M. Page and acknowledged by Mr. Davies.

A vote of thanks to the Officers and Council, having been proposed

DR. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 18, 1889, TILL MARCH 20, 1890. CR.

	£	s.	d.	£	s.	d.
Balance at Bank March 18th, 1889	1,831	17	9			
,, in hands of Treasurer	1	12	9	1,833	10	6
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 18th, 1889, to March 19th, 1889.						
26 Life Compositions at £20	520	0	0			
141 Admission Fees at £4	564	0	0			
32 Subscriptions for 1887 at £2	64	0	0			
88 ,, ,, 1888 at £2 2 ,, ,, ,, at £1	178	0	0			
344 ,, ,, 1889 at £2 4 ,, ,, ,, at £1	692	0	0			
795 ,, ,, 1890 at £2 27 ,, ,, ,, at £1	1,617	0	0			
1 ,, ,, 1891 at £2	2	0	0	3,637	0	0
Sale of Journal and Index				377	3	0
Subscriptions for Proceedings of Royal Society				10	0	0
,, from Institute of Chemistry				6	5	0
,, from Society of Public Analysts				4	4	0
Year's Dividends on £4,000 Converted 3 per cent. Consols				109	13	9
Six months' Dividends on £5,600 Metropolitan Board of Works 3½ per cent. Stock	95	11	0			
Six months' Dividends on £6,130 Metropolitan Board of Works 3½ per cent. Stock	104	12	0	200	3	0
Year's Dividends on £788 London and North Western Railway Debenture Stock				30	14	6
				6,208	13	9
Assets.						
Balance at Bank	2,035	9	7			
,, in hands of Treasurer	0	13	0			
3 per cent. Consols	4,000	0	0			
Metropolitan Board of Works 3½ per cent. Stock	6,130	0	0			
London and North Western Railway Debenture Stock	788	0	0			
	12,954	2	7			

	£	s.	d.	£	s.	d.
Expenses on Account of the Journal.						
Salary of the Editor, 1 qr. £62 10s., 3 qrs. £75	287	10	0			
Salary of the Sub-Editor	150	0	0			
Postages of Editors	3	19	3			
Fees to Abstractors	285	3	9			
Periodicals for use of Abstractors	21	16	0			
Printing of Journal	1,255	4	6			
Distribution of Journal	307	4	9	2,310	18	3
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
,, Clerk and Library Attendant	62	0	0			
Books and Periodicals	236	16	1			
Binding	34	2	10			
Bookcases	37	10	0	420	8	11
Printing Authors' Copies				43	11	0
Printing and Distribution of Abstracts of Proceedings				177	4	7
Banding and Distribution of Proceedings of the Royal Society				4	9	6
Miscellaneous Printing				89	4	0
Stationery				40	2	2
Inhabited House Duty and Income-tax				8	1	3
Heating apparatus				34	5	0
Carpeting				25	17	5
Repairs				10	4	9
Honorarium and other Expenses connected with Faraday Lecture				39	14	6
Collector's Commission on Subscriptions				181	17	0
Treasurer's Stamps and Drafts, and Charges on Drafts				5	12	3
House Expenses.						
Providing Refreshments	18	4	0			
Heating the Building (coals)	19	8	0			
Lighting ,, (gas)	49	7	3			
Cleaning ,,	20	0	0			
Petty House Expenses	8	17	1			
House Porter's Wages	58	10	0			
Gratuity to Gate Porter	2	2	0	176	8	4
Honorarium to Treasurer's Assistant				10	0	0
Treasurer's Petty Cash Disbursements				0	19	9
Purchase of £530 Metropolitan Board of Works 3½ per cent. Stock				598	12	6
Balance at Bank	2,035	9	7			
,, in hands of Treasurer	0	13	0	2,036	2	7
				6,208	13	9

Audited, with vouchers, and found correct.
March 22nd, 1890.

ROBERT H. DAVIES.
BERNARD DYER.
R. J. FRISWELL.

TREASURER OF THE CHEMICAL SOCIETY IN ACCOUNT WITH RESEARCH FUND.
FROM MARCH 18TH, 1889, TILL MARCH 20TH, 1890.

Dr.		£	s.	d.	Cr.	£	s.	d.
1889.								
Mar. 18.	Balance at Bank	464	16	4	Grant to W. H. Perkin, Jun.	50	0	0
	Dividends on £4,000 Metropolitan Board of Works 3½ per cent. Stock	136	10	0	Grant to R. Meldola	50	0	0
	Dividends on £1,000 North British Railway 4 per cent. Stock	39	0	0	Balance at Bank	540	6	4
		£640	6	4		£640	6	4

Assets.	£	s.	d.
Metropolitan Board of Works 3½ per cent. Stock	4,000	0	0
North British Railway 4 per cent. Stock	1,000	0	0
Balance at Bank	540	6	4
	£5,540	6	4

Audited, with vouchers, and
found correct,
March 22nd, 1890.

ROBERT H. DAVIES.
BERNARD DYER.
R. J. FRISWELL.

by Mr. Carteighe and seconded by Professor Ramsay, was acknowledged by Professor J. M. Thomson.

Mr. Warington moved that thanks be tendered to the Editors, Abstractors and Librarian; Mr. Pickering seconded the motion; Mr. Groves replied.

Mr. T. Fairley and Mr. W. Thorp having been appointed scrutators, a ballot was taken, and as result the following were declared elected as Officers and Council for the ensuing session:—

President: W. J. Russell, Ph.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, C.B., D.C.L., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, Ph.D., F.R.S.; Sir Lyon Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: Dr. A. Crum Brown, F.R.S.; G. Carey Foster, F.R.S.; W. N. Hartley, F.R.S.; J. W. Mallet, M.D., F.R.S.; J. Emerson Reynolds, M.D., F.R.S.; Robert Warington, F.R.S.

Secretaries: H. E. Armstrong, Ph.D., F.R.S.; J. Millar Thomson, F.R.S.E.

Foreign Secretary: F. R. Japp, LL.D., F.R.S.

Treasurer: T. E. Thorpe, B.Sc., F.R.S.

Ordinary Members of Council: Henry Bassett; Norman Collie, Ph.D.; C. F. Cross; Wyndham Dunstan, M.A.; John Ferguson, M.A.; E. Kinch; Raphael Meldola, F.R.S.; M. M. P. Muir, M.A.; F. J. M. Page, B.Sc.; S. U. Pickering, M.A.; R. T. Plimpton, Ph.D.; Thomas Purdie, B.Sc.

The Obituaries will appear in the June number of the Journal.

OBITUARY NOTICES.

WARREN DE LA RUE, born in Guernsey on the 18th January, 1815, was the son of the late Mr. Thomas De La Rue, founder of the firm of Thomas De La Rue & Co., Bunhill Row, London, well-known as manufacturers of stationery, Government stamps, bank notes, &c.

After having received his education at the College of St. Barbe, Paris, Warren De La Rue, whilst yet a lad, entered his father's business, where his special talents found a fertile field for activity. The keen interest in chemistry and physics which he evinced at an early age met with every encouragement from his father, and with great enthusiasm he devoted his leisure to their study, accompanied by experiments in the laboratory, in which, as occasion arose, the physical apparatus was devised by himself, and made by his own hands. As no other opportunities were available in those days, he had to acquire his knowledge in these respects entirely by private study; and he had the satisfaction of making practical use, in manufacturing processes, of the knowledge acquired in these scientific pursuits. His acquaintance with electricity led to an early employment of what was then the recent discovery of Jacobi and Spencer; and the practical application of galvanoplastics or electrotyping, in the factory at Bunhill Row is probably one of the first on record.

Although chemistry and physics were his favourite studies, he manifested a marked aptitude for mechanics; one of his great achievements in this direction was the construction of the first envelope machine, of which Mr. Edwin Hill and he were the joint inventors, and which was one of the engrossing attractions in the International Exhibition of 1851.

Notwithstanding his business occupations, he found time to go through a course of practical chemistry in the then recently established College of Chemistry, and this led to an intimate and lifelong friendship with Professor Hofmann, with whom he subsequently became associated in the drawing up of the Report in the Chemical Section of the Great Exhibition of 1851. While at the College of Chemistry, he finished his chemical investigation of the colouring matter of cochineal, which was published in the Chemical Society's Memoirs, 1845. About this time he also began to take an active interest in the pursuits of the Microscopical Society, and subsequently became much engrossed in Astronomy. Being gifted by nature with a remarkable sense of neatness and exactitude in work, associated as it was with great aptitude for mechanics and skill in drawing, he felt himself especially attracted to practical astronomy. At first, he directed his attention to the improvement of the contrivances for constructing reflecting telescopes, and this resulted in the erection at Canonbury, Islington, of a small observatory, with a fine 13-inch Newtonian reflector mounted equatorially after his own designs, and made in his own workshops. The perfection he attained in the casting, grinding, figuring, and polishing of the mirror were much appreciated by those specially interested in such work. At the outset, he occupied himself with accurate micrometrical measurements and graphic observations, in order to delineate the planets, which enabled him to produce exquisite drawings of Jupiter, Saturn, and Mars; these he outlined on steel, and, after being finished by the engraver under his personal directions, they were printed for private distribution. Thus engaged, the employment of photography for such purposes suggested itself to him, and after working out the photographic processes so as to make them available, his efforts were crowned by the production of the well-known beautiful photographs of the moon.

In 1857, the telescope was removed to a larger observatory, which he erected at Cranford, Middlesex, where he then resided, and for years the resources of this observatory were devoted to the steady development and study of celestial photography and its application to the recording cf astronomical phenomena. Although absolute priority is not claimed for this application of photography, Warren De La Rue was certainly the first to obtain automatic pictures of the moon and sun sufficiently delicate in their detail to serve for precise micrometrical measurement; these measurements he made with a micrometer which he invented for this purpose, thus affording numerical data for the advancement of our knowledge of the physical character of these bodies. The adaptability of photography for astronomical purposes having thus been demonstrated, De La Rue, in 1855, at the suggestion of Sir John Herschel, designed and planned the photoheliograph, which, with aid from the British Association, was constructed and mounted at the Kew Observatory in 1857 for the purpose of taking photographs of the sun. With this instrument, he joined the Himalaya Eclipse Expedition to Spain in 1860, and took charge of the photographic station erected at Rivabellosa. He was successful in obtaining a series of photographs of the total eclipse of the sun on July 18th of that year, and the outcome of these photographic results formed the subject of the Bakerian lecture delivered by him at the Royal Society, April, 1862. Henceforward, the apparatus and means for recording by photography became a recognised part of the equipment for the observation of solar eclipses. In 1865, in conjunction with Professor Balfour Stewart and Dr. B. Loewy, De La

Rue published at his own expense, for private circulation, "Researches in Solar Physics," Part I, in which various conjectures respecting the theory of sunspots are fully discussed. In 1866 Part II, and in 1868 an Appendix to Part II, of these researches were issued in the same manner. All were published in the *Philosophical Transactions of the Royal Society* for 1869 and 1870 as "Researches in Solar Physics: I. Heliographical Positions and Areas of Sun Spots, observed with the Kew Photoheliograph during the Years 1862 and 1863. II. The Positions and Areas of the Spots observed at Kew during the Years 1864, 1865, and 1866, also the Spotted Area of the Sun's visible Disk from the commencement of 1832 up to May, 1868." De La Rue also took an active part in the preparation for the photographic observation of the transit of Venus in 1874. The photoheliograph, after having been employed for some months at Cranford, was remounted at Kew, where it was regularly at work under his direction until 1873. It was then kept for some time at Greenwich, and, finally, re-erected at Kew in 1882 in order to observe the sun spots on Schwabe's methods, for which purpose it is still employed.

Although enjoying uninterrupted good health for many years, he now began to find that the night watching in the Observatory became more irksome, and he no longer felt able to undergo the fatigue and exposure entailed by such work. For this and for other reasons, he gave up his residence at Cranford, and returned to London. The observatory having to be dismantled, he presented, together with a quantity of other valuable apparatus, his equatorial telescope to the University of Oxford. This, under the direction of Professor Pritchard, in the new University Observatory, has since been chiefly employed in taking photograms of the moon, with the view of determining by the discussion of micrometrical measurements the inequality in the moon's rotation, and in determining by means of photography the distance of 61 Cygni and other fixed stars. In order that this work might be more effectually carried out, De La Rue made a liberal annual contribution for four years towards the payment of an assistant.

Having retired from business in 1869, he returned to it on the death of his younger brother William in 1870; but although head of the firm, he henceforward never took a very active part in the conduct of the business, and finally retired altogether in 1880.

As early as 1836, De La Rue had published a paper on Voltaic Electricity, and he now resolved again to take up this branch of science. Having, meanwhile, in conjunction with his friend and collaborateur, Dr. Hugo Müller, invented the chloride of silver battery, he fitted up a private physical laboratory, where, by means of this remarkably steady and convenient source of electricity, researches were made on the electrical discharge in the atmosphere as well as in various other gases at ordinary pressure, on vacua in exhausted tubes, and in the study of the nature and phenomena of the electrical arc. The battery which served for this purpose gradually attained vast proportions, and ultimately became the most extensive ever grouped in series. In 1879 it consisted of 11,000 cells, and in 1881 as many as 14,600 were in action at one time. An account of the results obtained is given in three memoirs printed in the *Phil. Trans. Roy. Soc.* for 1878 and 1880. These papers, from the variety of their contents, their great accuracy, and their splendid illustrations, form an important contribution to science. On June 21, 1881, he gave a memorable lecture at the Royal Institution, in which the construction of the battery was explained, and the phenomena of the discharge exhibited in a series of brilliant experiments. For this purpose, a new battery of 14,400 cells was especially set up, and amongst the results elucidated on this occasion was a demonstration that the maximum brilliancy of the aurora borealis would probably be at the height of about 37·67 miles; that at the height of 81·47 miles the appearance would be pale and faint, and that at 240 miles no electric discharge would take place.

The great range of his scientific attainments and pursuits brought him into intimate connection with many of the learned Societies, and he took an active part in their work, ever ready to give his assistance, whether by undertaking official work, or by promoting some scientific object with an unstinted liberality. He was in truth a characteristic example of what is specifically an English product, the man who, engaged in business and taking his share of public work, also successfully promotes science.

After acting for some time as Honorary Secretary of the Royal Astronomical Society, he was also its President from 1864—1866. He was for many years President of the London Institution, and became Secretary of the Royal Institution in 1878, which office he filled until 1882, when he retired on account of failing health.

He was elected a Fellow of the Royal Society in 1850, and was repeatedly Vice-President.

Warren De La Rue was one of the original members of the Chemical Society; and from 1867—1869, and again from 1879—80, he was its President.

De La Rue's scientific work has been embodied in papers and memoirs, which will be found in the *Transactions* of the Royal, Astronomical, Chemical, and other societies, and his labours have not escaped recognition by his scientific contemporaries abroad. He had been a corresponding member of the Imperial Academy of Sciences, St. Petersburg, of the Academy of Sciences, Institute of France, the

Royal Society of Upsala, an honorary member of the German Chemical Society, Berlin, and member of other learned societies. He was also a Knight of the Legion of Honour, a Commander of the Order of St. Maurice and St. Lazarus, and a Knight of the Brazilian Order of the Rose.

He died, after a short illness, on Good Friday, the 19th of April, 1889.

Michel Eugène Chevreul, born, on the 31st of August, 1786, at Angers, where his father was a leading physician, was educated at the École Centrale of his native town. At the age of seventeen, he went to Paris, and entered Vauquelin's chemical manufactory, in which establishment he afterwards held the position of director of the laboratory. In 1813, he was called to the Chair of Chemistry at the Lycée Charlemagne, and later on, he became Director of the Dyeing Department and Professor of Dyeing at the Tapestry Works of the Gobelins. His well-known researches on the laws relating to contrasts of colour were carried out at this time. In 1830, he succeeded his former master Vauquelin as Professor at the Natural History Museum, and in 1864, he was appointed Director of the Museum at the Jardin des Plantes, a post from which he retired in 1879, although he still retained his professorship.

In 1886, his hundredth birthday was celebrated in Paris with public rejoicings. He died on the 9th of April, 1889.

Of M. Chevreul's numerous researches, the best known are those dealing with the animal fats. The results of these investigations are given in a collected form in his great work, "Recherches chimiques sur les corps gras d'origine animale." Up to that time, chemists had regarded the soaps as combinations of fats with alkalis, but Chevreul having ascertained the composition of stearin and cleïn, and isolated and studied stearic acid and oleïc acid (all of them names which we owe to him), was able to explain the process of saponification. Apart from the vast scientific importance of this work, it had an immediate practical outcome in the stearin candle manufacture; these candles, first prepared by M. Chevreul, soon superseded the objectionable tallow dips of earlier times.

This happy blending of the scientific and the practical was frequently illustrated in M. Chevreul's investigations. Thus the technical excellence of the Gobelins tapestries, both in colour and in all that relates to stability of colour, is largely due to his efforts. His work, "De la loi du contraste simultané des couleurs et de l'assortiment des objets coloriés," embodying the researches already referred to, was published in 1829. Another work on a similar subject, "Théorie des effets optiques que présentent les étoffes de soie" (Lyons, 1846), contains lectures which M. Chevreul delivered at Lyons at the request of the Ministry of Trade and Agriculture.

His investigations cover the whole ground of chemistry, branching out into physiological chemistry, hygiene, and physics.

M. Chevreul was elected a Member of the French Academy of Sciences in 1826, a Foreign Member of the Royal Society in the same year, and of the Chemical Society in 1849. He received the Copley Medal of the Royal Society in 1857.

JOHN DALE, born in Birmingham on May 11th, 1815, was educated in Birmingham and Warwick. His school days at an end, John Dale went to Denbigh, where he was apprenticed to a chemist and druggist; later on he removed to Rhyl, where he had access to a number of chemical and pharmaceutical books, and there laid the foundation of his chemical knowledge.

He next proceeded to Manchester, where from 1833 to 1835 he acted as assistant to a Mr. Ansell, a chemist and druggist, a member of the Society of Friends, who was also an acquaintance of the renowned John Dalton; Ansell at that time being the only dealer in chemical apparatus in Lancashire or Cheshire. Under the circumstances, it was quite natural that Dale should soon make the acquaintance of Dalton, an acquaintance which soon ripened into friendship, for John Dale became Dalton's pupil. Urged on by the enthusiasm and genius of his master, Dale not long after this commenced a course of lecturing on chemistry in all the principal towns of Lancashire. He received from Dalton especial commendation and, indeed, compliment on his skilful and original lecture illustrations.

There now followed another slight change in a temporary removal to Altrincham. This, however, was soon succeeded by his return to Manchester, where a shop was taken in St. Mary's Gate, and it was during this period that Dale made the acquaintance of Mr. Thomas Roberts, with whom, some years later on, he entered into partnership. In the interim he became manager of a calico print works in Ardwick, and continued his duties in that capacity up to the year 1852, when he went to Cornbrook and started with Mr. Roberts the chemical works which under his directorship became famous and made widespread the name of the firm of Roberts, Dale, and Co. This brings us to about the year 1854, when the staple trade of the firm was wood extracts and British gum. About this period, the paperhanging trade began to develop rapidly, and Dale introduced a much greater variety of colours than had been hitherto employed; amongst them a superior class of chrome yellows, and also lakes made from wood extracts. Shortly after, the manufacture of oxalic acid from sawdust, by heating this material with a mixture of potash and soda, was commenced at the Warrington works, which later on was managed by Dale's eldest son, John. The working of the new process, which marked a very important epoch in chemical industry, was undertaken in conjunction with J. D. Pritchard, and subsequently brought to further perfection by Dale, and carried on until such time as potash became sufficiently cheap to justify its sole use. Those who recollect the reports issued at that time of this process will remember that the mode of separating the alkaline salts was based on the fact that whilst the potash salt was soluble the soda salt was insoluble in water. It is exceedingly probable that, in connexion with the operations of this process, vacuum filtration on an industrial scale was employed for the first time; such an accelerated method of filtration being, of course, highly desirable in connection with the separation of the oxalic acid solutions from gypsum, when the calcium oxalate obtained by causticising the insoluble oxalate of soda with boiling milk of lime came to be treated with sulphuric acid. No doubt John Dale was perfectly aware of Gay-Lussac's reaction, discovered in 1829, by which carbohydrates and celluloses fused with potash yield oxalic acid; and he founded upon it the successful commercial process referred to. Just about this period, too, the manufacture of solid caustic soda was commenced and successfully prosecuted. The record now brings us to the year 1858, when Perkin discovered mauve. In conjunction with Caro, who was engaged as chemist about the years 1860 to 1861, Dale now endeavoured to discover an oxidising agent for preparing mauve as effective as potassium dichromate, and found that copper sulphate, in conjunction with alkaline chlorides, answered the purpose.

In the meantime, C. A. Martius had been engaged as chemist at the Warrington works, and came there from Hofmann, in whose laboratory he had acquired a sound theoretical knowledge of the then recently discovered aromatic bases, such as phenylenediamine, dimethylaniline, &c. He was at once set to work by Dale, with the object of preparing new colours from such aromatic bases, through the medium of nitrous acid obtained from nitrite of soda. From this course of experiments directly sprang the manufacture of Manchester brown ("Bismarck brown"), and Manchester yellow ("Martius yellow").

Ordinary aniline yellow or amidoazobenzene ("fast yellow") was next placed in the market.

Somewhat before this date, John Dale had commenced the manufacture of picric acid, first from Australian gum, and later on more advantageously from commercial carbolic acid. Then followed the manufacture of aurin, which was also commenced about this period.

John Dale's youngest son, R. S. Dale, was now set to work by his father upon the aurin process, which he perfected, and, in conjunction with Schorlemmer, wrought out the theoretical development of the subject; together they also succeeded in converting aurin into pararosaniline, thus establishing it as a triphenylmethane-derivative (this Journal, 1885, 476). Other aniline colours were later on prepared in Dale's laboratory, and afterwards manufactured in the works. Among the names of the noted chemists who were engaged in Dale's laboratory were those of Caro, Martius, Schad, Leonardt, and Kopp.

Not only was the mind of Dale fertile and resourceful as regards manufacturing methods, but his ardent study of the pure science stood him in good stead as regards analytical and valuation methods, and it is a fact that he mainly devised his own analytical processes. During the last four or five years Mr. Dale's health had been failing, but his interest in the later developments of all branches of chemical industry never flagged in spite of this. Most of the chemists connected with the paper-making, calico printing, and textile industries applied to him at one time or another for counsel and advice, and never failed to obtain the assistance they desired. He died May 31st, 1889, and it may be truly said that, whilst Joule stood pre-eminent in physical research, and Dalton in chemical theory, John Dale, Dalton's pupil, must take rank as a typical representative of the successful application of chemical science to chemical industry.

ANTON GEUTHER was born on the 23rd of April, 1833, at Neustadt, in the Duchy of Saxe-Coburg. In 1863, at which time he was a "Privatdocent" at the University of Göttingen, and Senior Assistant in Wöhler's laboratory, he was called to the University of Jena, where he spent the remainder of his life. He died on the 25th of August, 1889.

Geuther's researches, which are numerous, deal both with organic and with inorganic chemistry; but perhaps his most important, and certainly his best known work is his discovery of ethylic acetoacetate and several of its derivatives. Every chemist knows how the reaction in which these compounds were obtained was studied almost simultaneously by Geuther, and by Frankland and Duppa; and it is perhaps fortunate that Geuther published his results in so inaccessible a periodical as the *Jenaïsche Zeitschrift*, since in this way they remained unknown to the two English chemists, who could thus attack, from a different point of view, and by independent methods, a problem which they might otherwise have been deterred from approaching.

Other well-known researches of Geuther's are his synthesis of acetal, the discovery of nitrosodiethylamine (the first instance of a nitroso-derivative of a secondary amine), of dehydracetic acid, and his method of preparing complex organic acids and ketones from sodium alcoholates, sodium hydrate, and carbonic oxide. It may also be mentioned that the first germ of the idea of "labile" modifications—a conception which now-a-days plays so important a part in interpreting the mechanism of various organic reactions—is contained in Geuther's writings.

In 1887, he published his "Lehrbuch der Chemie, gegründet auf die Werthigkeit der Elemente."

Professor Geuther was elected a Foreign Member of the Chemical Society in 1888.

James Prescott Joule was born on December 24th, 1818, at Salford. His father was a brewer in that town, carrying on a business which had descended to him from his father, and which was later on managed by Joule and his brother. As a child, Joule was delicate, and did not, therefore, go to school, his education being conducted by his mother's sister and by tutors, until he reached his 16th year. He was then sent with his brother to study physical science under Dalton, who was President of the Manchester Literary and Philosophical Society, and received pupils at the Society's rooms. Here Joule became first acquainted with physical apparatus, and speedily commenced making experiments on his own account, chiefly in the branch of magnetism. These were the beginning of Joule's life-work, which, though it is commonly considered to belong to the domain of physics, has nevertheless exercised an enormous influence on the progress of chemical science.

In his first work on magnetism, published at the age of 19, he constructed electro-magnetic machines of improved form, and by means of these was able to determine the value of the limit of magnetisation communicable to soft iron by the electric current. He also compared the values of solid iron cores and bundles of iron wires for the electro-magnetic machine, and succeeded in constructing electro-magnets of greater lifting power than any previously obtained.

At that time the numbers used to characterise electric currents were arbitrary and vague, and Joule's next efforts were applied to devising a scientific and at the same time convenient method of expressing the results. He based his proposal on Faraday's recently-discovered law of electro-chemical equivalents, taking as unit the quantity of electricity necessary to decompose 9 grains of water, 9 being then supposed to be the molecular weight of water.

In 1840, led by experiments made with the object of improving voltaic apparatus, he turned his attention to "the heat evolved by metallic conductors of electricity and in the cells of a battery during electrolysis." The results of this work are summed up in the following laws:—"In a metallic conductor carrying an electric current, the quantity of heat evolved in a given time is always proportional to the resistance which it presents, whatever may be the dimensions or kind of the metallic conductor;" and also that "The quantity of heat evolved is proportional to the square of the quantity of electricity passing in a given time."

During the same year he pointed out that the heat generated in a wire conveying a current of electricity is *part* of the heat of chemical combination of the materials used in the voltaic cell, and that the *remainder*, and not the whole heat of combination, is evolved within the cell. In the two years following he continued these investigations, and showed that the sum of the heat produced in all parts of the circuit during voltaic action is proportional to the chemical action which goes on in the voltaic pile, and that, further, the quantities of heat evolved by the combustion of equivalents of the elementary bodies are proportional to the intensities of their affinities for oxygen.

To another paper on this subject, read before the Manchester Literary and Philosophical Society on January 24th, 1843, an especial chemical interest is attached, as establishing the heat equivalence of chemical action. Dulong had already determined the amount of heat evolved during combustion, but did not compare this with the heat evolved by the same combustion in the battery or elsewhere, and Joule's discovery, described in the above paper, was that the heat which disappears during separation of the chemical elements was equal to that which made it appearance during their combination, on the principle that action and reaction are equal and opposite. This was the discovery which proved that chemical action was due to the clashing of the atoms, and that the same laws applied to those atoms singly as they did to them when taken in the aggregate, thus showing that chemistry was a branch of molecular physics.

In the early part of 1843 he was further able to announce that the magneto-electric machine enables us to convert mechanical power into heat, and at the meeting of the British Association at Cork, on August 21st, 1843, he read his paper—"On the Calorific Effects of Magneto-electricity, and on the Mechanical Value of Heat," in which he shows experimentally that heat is *generated* by the electro-magnetic machine and not merely *transferred* from some source. An account was also given of a further series of experiments conducted with the view of discovering whether any constant ratio existed between the heat generated and the mechanical power employed to produce it. From one set of experiments he obtained the result that 838 foot lbs. are equivalent to the quantity of heat capable of raising 1 lb. of water through 1° Fahrenheit. At the close of the paper he stated that he had also succeeded in proving the generation of heat by forcing water through narrow tubes, and that 1 degree of heat per lb. of water was obtained from a force capable of raising 770 lbs. to the height of 1 foot.

This was the first determination of the mechanical equivalent of heat, but Joule subsequently obtained similar results in different ways. Concerning these, and his other numerous researches, space does not permit of a detailed consideration. The number of his various papers amounts to no less than 115, and have been reprinted by the Physical Society of London in two volumes, the second containing the papers published jointly with Dr. Scoresby, Sir Lyon Playfair, and Sir William Thomson.

Joule's apparatus was, for the most part, constructed by himself. As an example of his ability in this respect, it may be mentioned that during his investigations he greatly felt the need of accurate thermometers, and in conjunction with Mr. Dancer, of Manchester, prepared the first English thermometers of any great accuracy.

The value of Joule's work cannot be better expressed than in the words of a writer in *Nature* for October 24th, 1889, "His work, taken as a whole, and without considering the relative importance to physical discoveries—that is to say, judged by the originality of the objects, and the means employed, the philosophic direction, the patient and persevering labour, and the results obtained—would be such as to place him in the front rank of philosophers. If account be taken of the importance and generality of his discoveries, as shown by their influence on the philosophical thought and material progress of the world, then, as the discovery of the law that energy is in the same degree indestructible and uncreatable as matter, it is with Newton and Dalton that he finds his place in the history of physical science."

Joule was of an extremely retiring disposition, and never came prominently before the public. He married, in 1847, Amelia, daughter of Mr. John Grimes, Comptroller of Customs, Liverpool. His wife died in 1854, leaving him a son and a daughter. He received honorary degrees from all the more important Universities, and was honorary fellow of many learned Societies, both at home and abroad. He received the Royal Gold Medal from the Royal Society in 1852, and the Copley Gold Medal in 1870, and the Albert Medal of the Society of Arts was delivered to him from the hands of the Prince of Wales in 1880. A pension of £200 was granted him from the Civil List, in recognition of his services, in 1878. He became a Fellow of this Society on the 1st of January, 1844, and remained a member till his death. He was also elected President of the British Association in 1873, but, owing to ill-health, he was unable to undertake the duties of the office, his place being taken by Professor A. W. Williamson. He died at his residence, Wardle Street, Sale, on the 11th of October, 1889, aged 71.

Benjamin Nickels was born in London on the 7th October, 1830; his father being an india-rubber manufacturer, the necessity for chemical knowledge in the early days of "vulcanising" gave the direction to the son's studies after leaving school. He associated himself with the Westminster Literary and Scientific Institution, of which he soon became the honorary secretary (1847), occasionally delivering elementary lectures on chemistry to his fellow-students. The discovery of gold in Australia opened out the prospect of useful employment as an assayer, and he established himself in Sydney, New South Wales, during the next few years, returning to Lambeth in 1856, and taking post as chemist in Bell's india-rubber factory, removing to Hooper's Telegraph Works at Mitcham, where he introduced an improved system of laying submarine wires, for which he took out a patent in 1858. This led to his subsequent engagement at Messrs. S. W. Silver and Co.'s india-rubber factory at Silvertown, where for several years he was employed as chemist. In May, 1866, he became public analyst in Bath, and did good service in advising the Town Council on the question of water supply after making the needful analyses. From 1869 to 1876 he was chemist at Messrs. Brooke, Simpson, and Spiller's dye works, first at Hackney Wick, removing to Greenford Green on the transfer of this establishment from Messrs. Perkin and Sons to the above-mentioned firm, and remaining on for other three years (1876 to 1879), when it passed into the hands of Messrs. Burt, Boulton, and Haywood. For the last ten years Mr. Nickels occupied himself as a general consulting chemist, frequently employed in the examination of coal-tar products, disinfectants, food and water analyses, and india-rubber samples, for which kind of work his previous training had especially qualified him. In January, 1882, in conjunction with Mr. W. G. Little, of Doncaster, he took out a patent for a composition for coating ships' bottoms, &c., in which the essential ingredient was acridine, obtained from heavy coal-tar oils. In 1885, Mr. Benjamin Nickels served on the jury of the International Inventions Exhibition (in Group XXI, India-rubber and Gutta-percha); and at various times wrote articles and gave evidence bearing upon the india-rubber manufacture. He died on the 13th November last, aged 59, of internal tumour, supposed to be the result of a fall, leaving a widow and several children, besides many personal friends, to mourn his loss.

James Walker Montgomery* was the son of the Rev. John Montgomery, M.A., Free Church Minister at Innerleithen, Peeblesshire, and was born there on 31st October, 1847. He was the eldest of three sons; the other two of whom survive. His early education was obtained at Innerleithen and at Edinburgh, where he attended the School of Arts. Turning his attention to chemistry, he entered the laboratory of Dr. Stevenson Macadam, Surgeons' Hall, Edinburgh, where he studied for about five years, acting latterly as his assistant. Proceeding to London, he spent two or three years as an assistant in the laboratory of Messrs. Johnson and Matthey, assayers.

Mr. Montgomery subsequently purchased and entered on a practice as an analyst at Stockton, which, however, proved disappointing, and thence, after a short time, he removed to Whitehaven, where, in 1872, he took over the analytical and consulting practice of Dr. E. G. Tosh, which he continued for the remaining 17 years of his life.

The practice was very extensive, and, as he also acted as chemist to several important iron works, his life became a very busy one. In 1878 he was appointed public analyst for the county of Cumberland, and, in 1872, for the county of Westmorland and the borough of Kendal, the duties of which offices he faithfully and conscientiously discharged to the last.

Unfortunately, the state of Mr. Montgomery's health in the latter years of his life, and the intense physical suffering which he bore silently and uncomplainingly, prevented the prosecution of chemical experiments and research—especially in the relations of chemistry to physiology and medicine, to which he had been previously inclined. His manliness and integrity won him universal esteem, which was shown by his election to several important offices, civic and masonic. He sat for several years on the Board of Trustees for the Whitehaven Town and Harbour Trust, as a representative of Lord Lonsdale, the Lord of the Manor.

Mr. Montgomery took a keen interest in agricultural matters, and delivered several lectures in connection therewith in the county. As an expert in iron analysis he gave evidence in several cases of importance.

Honourable and straightforward himself, he had a strong sense of the importance and status of his profession as an analyst.

He died after a severe illness, patiently borne, on February 14th, 1889; his death causing intense grief, not only to his family circle, but to many sincere friends who were very deeply attached to him. He is survived by his widow and son.

David Page, M.D., F.I.C., the eldest son of the late David Page, LL.D., F.R.S.E., Professor of Geology in the College of Science,

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* Notice of his death received since the Anniversary Meeting.

Newcastle-on-Tyne, was born in Edinburgh, in the year 1846. He studied science at the University of Edinburgh, in the years 1862–64, and worked in the Chemical Laboratory, under the direction of Sir Lyon Playfair, who then held the Professorship. He left the University to enter upon an engagement as chemist to the Gatebeck Gunpowder Mills of Messrs. Wakefield and Co., near Kendal, and in that capacity he was joint author with one of the partners, the late A. D. Keightley, of a paper on the solubility of potassium nitrate and other salts, which is published in the Journal of the Chemical Society. This investigation was the foundation of an important technical process. He subsequently re-entered the University, and became one of the most distinguished students in the Faculty of Medicine, gaining no fewer than 15 gold medals in various subjects of the curriculum, including the medal for the best thesis in his year of graduation. The subject of this work was an experimental research on death by suffocation. For some little time he was engaged in private practice at Kirkby Lonsdale, in Westmorland, and during this period he had to give evidence at Lancaster Assizes, in a trial for child-murder, and support his statements by giving a detailed account of the work recorded in his thesis. His evidence proved to be conclusive. He afterwards moved to Kendal, on being appointed Medical Officer of Health for the county of Westmorland. During his term of office many beneficial reforms in the sanitary condition of the county were effected, particularly in the matter of water supply and house drainage. His chemical work at this period consisted chiefly of water analysis, in which he became an expert, possessing an accurate and extensive knowledge of the composition of the natural waters of various portions of his district. He next entered the Civil Service as one of the Medical Officers under the Local Government Board, Whitehall, and became Vaccination Inspector for the Northern Counties of England, choosing Lancaster as his head-quarters. At the same time, his various abilities in other departments of sanitary medicine were made use of at Whitehall, and a number of districts throughout the kingdom. His principal official reports comprise one on the sanitary condition of Margate; on the cause of death by poisoning, at a wedding breakfast at Carlisle, which was traced to an American ham, of which some of the guests had partaken; and the investigation of an outbreak of typhoid fever at South Hetton, in Durham, which occurred in the summer of 1889. The latter case possessed some remarkable features, and was the subject of a particularly able piece of research. It was proved beyond question that the epidemic was caused by the water supply, and that a well, believed and strenuously asserted to be a source of unpolluted water, was contaminated by farm middens, standing upon elevated ground, some mile and a half distant. The drainage water found its way into the well through a fissure in the limestone rock. He was appointed the external Examiner in Medical Jurisprudence in the University of Edinburgh in 1889.

Dr. Page was a man of great energy and keen mental activity. Everything which he undertook was performed not only as a matter of duty, but to the very best of his ability. His chemical work was executed with extreme care and accuracy, and at the same time with unusual rapidity. He possessed considerable literary skill, and could write reports and correspondence in well chosen language, clearly and tersely expressed, without hesitation or correction. With a happy disposition, a kindly spirit, a genial manner, and a ready wit, he was at all times a delightful companion.

For some time past he suffered occasionally from headache, supposed to be induced by much railway travelling, but latterly occasional symptoms, such as a slight numbness in the right hand and foot, and fits of giddiness, necessitated a medical consultation.

In January last he was told to apply for six months' leave of absence, and was strictly enjoined to keep himself, as far as he could, from brain work. In order to recruit his health, and with the full concurrence of his medical advisers, it was proposed that he should take a sea voyage. He was actually on a visit to the writer to make arrangements for joining in a trip to the Mediterranean, when he was seized with an illness, which rapidly developed, and terminated fatally the following day. His death, which occurred at 36, Waterloo Road, Dublin, on the 20th February, proved a terrible shock to all his relations and friends. The cause of death was a tumour on the brain, probably the growth of several years. He was twice married, and has left a widow and seven children to mourn their loss.

Dr. ROBERT ROMANIS, Chemical Examiner to the Burma Government, and Professor at the Rangoon College, was born in 1854, being the son of the late Mr. C. S. Romanis, formerly of St. Petersburg, but latterly residing in Leith. He was educated at Edinburgh University, where he took his D.Sc. degree, and in Germany, and at one time was on the staff at Clifton College. A short time after this, Dr. Romanis proceeded to Burma, on his appointment to the science mastership of the Rangoon High School, which subsequently became the Government College. The following is taken from the *Rangoon Times*:— "We regret to announce the sudden death at nine o'clock this morning, of cholera in its most acute form, at his residence in Sandwith Road, of Professor Romanis, D.Sc., F.G.S., Rangoon College, Chemical Examiner to the Government, and a captain in the Rangoon Volunteers. Originally appointed Teacher of Natural Science at the High School, he joined the Service in July, 1878, being gradually promoted to the high position he had obtained through services that met with the entire approbation of all that knew him and his work. Of retiring disposition, he ever abstained from the little disputes that occasionally vex the local mind; and of him it may be said that he has passed away universally beloved and regretted. It will be long before his post is so ably filled; before he is forgotten in the community that sorrows in his early death, or among his pupils and associates. It is to be lamented that, owing to the suddenness of the event, and to the fact that, most of the educational establishments being broken up, it will be impossible for many, who would otherwise be there, to pay the last tribute to a sincere and valued friend." During the Burmese war he was on the staff of General Prendergast, and made a special report on the resources of the recently acquired territory. He died in Rangoon of cholera, in the early part of 1889. He was a Fellow of the Linnæan and Chemical Societies, and a Fellow of the Institute of Chemistry.

Dr. **Edmund Ronalds** was born in Canonbury Square, London, in the year 1819. His father, Edmund Ronalds, was a merchant in London, whose brother, Sir Francis Ronalds, was knighted a few years ago in recognition of his connection with the origin of the electric telegraph. After leaving school in England, Edmund Ronalds went abroad and studied successively at Giessen, Jena, Berlin, Heidelberg, Zurich, and Paris. At Giessen, he was the fellow student of Kopp, Fresenius, Will, and other well-known chemists. In 1840, he returned to England, and held the lectureships in chemistry successively at St. Mary's Hospital and the Middlesex Hospital. In 1849, he was appointed Professor of Chemistry in Queen's College, Galway. In 1856, he gave up his professorship, and took over the Bonnington Chemical Works, where the products of the Edinburgh Gasworks were worked up. About 10 or 12 years ago, he gave up business, and occupied himself with researches in his private laboratory, where he made any chemist welcome who was in want of laboratory accommodation. Of the numerous chemists who, for one reason or another, have resided in Edinburgh during the last 30 years, there are few who have not occasion to remember him with gratitude and affection. He was for several years in very poor health, and tried various changes of climate, but with no permanent good effect, and he died on 9th September, 1889, leaving a widow and six children.

David Waldie was born in Linlithgow, in Scotland, about the year 1810, his father being a chemist and druggist of that town. He was educated in Edinburgh as a surgeon, where he took the diploma of the Royal College of Surgeons, and subsequently he practised as a medical man for some time in Linlithgow. He early showed a strong inclination for chemical studies, and at this period undertook original researches on the combustion of various substances in different gases, publishing papers on the subject in the *Philosophical Magazine*. His experiments are referred to in "Gmelin's Handbook to Chemistry," **2**, 30—31. He succeeded Dr. Brett as chemist to the Liverpool Apothecaries' Company.

Among the medicinal preparations made at the laboratory of the Apothecaries' Hall was so-called spirit of chloric ether. This was manufactured in a crude manner by distilling alcohol with chloride of lime. He introduced an improved method of manufacture by separating the chloroform and dissolving it in a known quantity of spirit. At this time, Sir James Simpson was investigating the properties of ether as an anæsthetic, and, being a friend of Mr. Waldie's, asked him if he could recommend anything better. He suggested chloroform, which, in Sir James Simpson's hands, produced such wonderful results.

In 1853 Mr. Waldie went to Calcutta, being sent out by the firm Messrs. Malcolm and Co. as experimental chemist. There he not only superintended the refining of borax and saltpetre at Goosery, but also carried out the manufacture of carthamim from safflower; the latter, however, was not pecuniarily successful. On Messrs. Malcolm and Co. relinquishing business, Mr. Waldie took over a chemical manufacturing business at Duckinsore, and also practised as an analytical chemist. This business he afterwards removed to Barnagore, and eventually to Cossipore, carrying it on up to 1887, when he sold it to its present proprietors.

He has been a Fellow of the Chemical Society since 1843, and was also a member of the Asiatic Society. About 1865, he commenced a protracted series of experiments, extending over some years, relating to the filtration of the Hooghly river water for the Calcutta water supply, the importance of which was acknowledged by the chief engineer to the Calcutta Waterworks, and a report of which was printed and also appeared in the *Proceedings of the Asiatic Society's Journal* in the years 1866–67.

XXX.—*Researches on the Germination of some of the Gramineæ.* Part I.

By HORACE T. BROWN, F.R.S., and G. HARRIS MORRIS, Ph.D., F.I.C.

CONTENTS.

No. of Section.		PAGE
(1.)	Introduction	459
(2.)	Structure of a grain of barley	461
(3.)	The visible changes which occur in the *embryo* and *endosperm* during germination	466
(4.)	The relation of the *embryo* to the *endosperm* that of a parasite to its host	474
(5.)	Development of excised *embryos* on foreign *endosperms*	478
(6.)	The starch-containing portion of the endosperm to be regarded as a store-house of *dead* reserve material; no residue of vitality being recognisable in its cells	478
(7.)	Cultivation of excised embryos on water	482
(8.)	Cultivation of excised embryos on nutrient solutions	483
(9.)	Growth of excised embryos on *starch*, and proof that an amylo-hydrolyst (diastase) is secreted by the growing embryo	489
(10.)	The secretion of diastase is localised in the "absorptive epithelium"	493
(11.)	The secretion of diastase increased by very dilute acid	494
(12.)	The secretion of diastase not stimulated by the presence of *starch*	495
(13.)	The secretion of diastase is inhibited by a readily assimilable carbohydrate	495
(14.)	The existence of a cellulose-dissolving enzyme (cyto-hydrolyst) in the germinating seeds of Grasses	497
(15.)	The cyto-hydrolyst, like diastase, is secreted by the "absorptive epithelium"	502
(16.)	The two varieties of diastase, their genesis, and distribution in the resting and germinating seed	505
(17.)	Distribution of diastase in the germinating seed	507
(18.)	The mother substance of "diastase of secretion" is principally derived from the endosperm	510
(19.)	Action of "diastase of secretion" upon ungelatinised starch	510
(20.)	A consideration of the origin of the hydrolytic enzymes of germinating grain	511
(21.)	The form in which the reserve starch, after transformation, enters the growing embryo, and a consideration of the metabolic changes which it there undergoes	513
(22.)	*Addendum.* A consideration of the recent hypothesis of G. Haberlandt that the aleurone layer secretes diastase during germination	520

(1.) *Introduction.*

THE complex metabolic processes which take place during the germination of seeds have attracted, from the time of Th. De Saussure, a large amount of attention both from vegetable physiologists and chemists: nevertheless at the present time we are far from possessing an exact knowledge of the mode by which the embryonic plant is enabled to appropriate any single one of the reserve materials stored up in cotyledon, endosperm, or perisperm.

It is true that the purely chemical phenomena attending the dissolution of at least one of the more important reserve materials, *starch*, and in a less degree of certain substances belonging to the obscure class of *proteïds*, are now fairly well understood; but our knowledge of the special physiological processes of which these chemical phenomena are an expression is still in the highest degree incomplete. The same cannot be said, however, of the histological and morphological sides of the subject, for, thanks to the unwearying and patient work of numerous observers, our knowledge of the minute structure and developmental history of some seeds is so complete as to form a perfectly safe basis upon which the physiologist and chemist can work.

There is an accumulation of experimental evidence tending to show that, during germination, the solid reserve materials of the seed are broken down and rendered soluble and diffusible under the action of *enzymes*, or soluble ferments,* which either appear for the first time during the progress of germination, or, if pre-existent in the resting seed, have had their activity much intensified.

Starch is undoubtedly broken down in this manner, and the work of Gorup-Besanez, S. H. Vines, J. R. Green, Schulze and Barbieri, and others, leaves little doubt that the reserve *proteïds* also owe their dissolution to the action of soluble proteïd-hydrolytic ferments. The evidence of the breaking down of cellulose by a special enzyme has, up to the present time, not been quite convincing, but, speaking generally, the more our knowledge of the chemical processes accompanying germination increases, the more evidence is forthcoming of the important *rôle* played by soluble ferments.

That the genesis of these enzymes is intimately connected with the growth of the embryo, is, we imagine, generally admitted, but beyond this we may be said to have no positive knowledge, and we are for the most part entirely ignorant, not only of the chemical origin and nature of the enzymes, but even of the particular part of the seed in which they take their rise, and of their mode of transference from part to part.*

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* For an explanation of the nomenclature employed in this paper, see Armstrong, this vol., p. 528.

The present investigation was undertaken in the hope of throwing some light upon these points, and of obtaining some experimental data to guide us where hitherto argument by inference has alone been possible; and since the key to many difficult problems in plant metabolism is to be sought in the germinating seed, it seemed

EXPLANATION OF PLATE I.

pi.	Inferior palea, consisting of—
ep.e.	External epidermis.
sch.	Schlerenchyma; sub-epidermal bast.
fv.	Vascular bundle.
chl.	Chlorophyll layer.
ep.i.	Inner epidermis.
per.e.	Outer layers of pericarp.
per.i.	Inner „ „
teg.	Testa.
ep.nucell.	Epidermis of nucellus.
t.ad.	"Aleurone-cells" of endosperm.
t.am.exs.	Depleted and compressed cells of endosperm.
t.am.	Starch-containing cells of parenchyma of endosperm.
scut.	Scutellum.
t.abs.	"Absorptive" and secretory epithelium.
proc.	Elongated parenchymatous cells of scutellum.
ksch.	Plumule-sheath.
$f._1$, $f._2$, $f._3$, $f._4$.	Leaves of plumule.
ax_1.	Primary axis: ax_2, ax_3, ax_4. Secondary axes.
tig.	Point of origin of the procambium strands which enter the scutellum, leaves, and radicles.
J.	Growing point of primary radicle.
cal.	Calyptrogen. (Root-cap).
col.	Coleorhyza. (Root-sheath).
ap.emb.	Appendage of embryo.
t.ph.	Sheaf-like cells: the remnant of the nucellus.
p.peric.	Dorsal portion of pericarp.
p.s.	Superior palea.
h.	A strand of tracheïdes.
ax.s.	Basal bristle.
x.	Meristematic portion of the hypocotyledonary axis, which is in greater part absorbed by the secondary radicles during their development.
f.p.	Funiculus.

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* The localisation of a special enzyme which brings about the hydrolysis of a glucoside present in the berries of *Rhamnus infectorius* has recently been beautifully worked out by Marshall Ward and Dunlop, who find that, whilst the glucoside resides in the pericarp, the enzyme which brings about its hydrolysis occurs only in the *raphe*. (See *Annals of Botany*, vol. i, p. 1, 1887.)

BROWN & MORRIS

probable that such an enquiry might increase our knowledge of some of the more important physiological processes of plant life.

As the chance of success by attacking these problems from a purely chemical point of view seemed very small, we have endeavoured, during the last few years, to put ourselves in a position, as far as possible, to approach them also from their biological side, and to make ourselves acquainted with the great mass of work carried on by previous observers which has any direct or indirect bearing on the subject of this paper. Although we have, during the progress of our enquiry, examined and experimented with the seeds of many of the Grasses, we shall in the first part of our paper confine ourselves almost entirely to the results obtained with *barley*, since, in the first place, the histology and developmental history of this grain have been more fully worked out than in the case of any other species of the Gramineæ; and, secondly, there seemed some hope of our results ultimately having some practical bearing on the large and important industry of malting, which is still in a purely empirical stage.

(2.) *Structure of a Grain of Barley.*

It will be necessary at the outset briefly to describe the structure of a grain of barley, which may be taken on the whole as a good type of the seeds of the natural order of plants to which it belongs. In doing this we shall not enter more into details than is necessary for a comprehension of the matters discussed in this paper, but must refer, for a full histological description, to the recent exhaustive monograph of Holzner and Lermer, "Beiträge zur Kentniss der Gerste," München, 1888, from which source the accompanying figure has been reproduced, but on a much diminished scale.*

The contents of the grain of barley at the period of maturity consist almost entirely of embryo and endosperm, which, taking their rise in the embryo-sac, have, during their development, almost completely displaced the tissues of the nucellus, ovule, and ovary. The only remnants of the nucellus which are recognisable in the ripe grain are the empty sheaf-like cells, *t.ph.*, Plate I, which spring from the funiculus, *f.p.;* and the epidermis of the nucellus which is continuous as a very attenuated layer of cells around both embryo and endosperm. Of the walls of the ovule, only the inner one persists, as a double layer of cells forming the *testa*, *teg.*, or true coating of the seed. The parenchymatous tissue of the ovary, which during the development of the embryo-sac is rich in starch, and in certain layers also in chlorophyll, is in great part displaced, leaving only its vestiges in the *pericarp, peric.*, which may be differentiated into endocarp, mesocarp, and epicarp.

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* See also W. Johannsen, "Développement et constitution de l'endosperme de l'Orge." *Résumé du Compte-rendu des travaux du Laboratoire de Carlsberg* 1884, p. 60.

Outside the pericarp are the inferior palea, *p.i.*, and superior palea, *p.s.*, which in the ordinary varieties of barley become permanently attached to the pericarp during the development of the ovary. The grain of barley, and in fact that of all species of the Gramineæ, is consequently a *caryopsis* or an *achene* with pericarp adherent to the seed-coat, for it includes the united products of both ovule and ovary.

To return once more to the endosperm and embryo, which, as we have seen, are both developed within the embryo-sac. The principal mass of the endosperm consists of thin-walled cells packed closely with starch-granules embedded in a very fine net-work of proteïd material,* *t.am.*, but in the peripheral portion is a triple or quadruple layer of cells, *t.ad.*, with thick and highly cuticularised walls. These cells, in transverse and longitudinal section, are roughly speaking rectangular in form, and constitute the so-called aleurone-layer of the endosperm. They are present in the seeds of all the Grasses, but vary much in form and arrangement; they are, however, always peripheral in position, and their contents consist mainly of spherical, closely packed, aleurone-grains and fat, embedded in a protoplasmic matrix in which a well-defined nucleus is recognisable. The aleurone-layer in barley, where it is in contact with the starch-containing cells, is generally represented, as has been already stated, by a triple or sometimes quadruple row of cells, but when traced downwards it changes its character in the portions surrounding the embryo, becoming a single layer of smaller cells, which gradually die away when followed towards the base of the grain. This modified aleurone-layer does not enter the embryo at any point, but is only in close contact with it.

Lying between the starch-containing portions of the endosperm and the embryo is a comparatively thick layer of emptied and compressed cells, *t. am. exs.*, belonging to the endosperm, the existence of which calls for a word of explanation. In the early stages of the development of the endosperm, the starch-containing cells at one time occupy nearly the whole cavity of the rapidly increasing embryo-sac, and the embryo, which arises in the apical end of the sac from the fertilised oosphere, is almost surrounded by the young tissue of the endosperm. The development of the embryo, except in its very early stages, before the disappearance of its suspensor, takes place wholly at the expense of the endosperm, and as its position becomes lateral, the whole embryo grows rapidly and encroaches upon the space occupied by the parenchyma of the endosperm, emptying its cells of their starch and protoplasmic contents. The cell-walls of the tissue, thus put under contribution, do not, however, share the fate of the cell-contents, but persist in the ripe grain as a belt of transparent cellular tissue, in which the individual cell-walls are not always distinguishable, owing to their extremely close adhesion. The appearance of this layer in some of the principal Grasses will be referred to in a future part of this paper.

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* These starch-containing cells of the endosperm possess a nucleus which, however, in the case of barley is somewhat difficult to recognise. We have found that the best way to demonstrate its existence in this and other seeds of the Gramineæ is to digest thin sections of the endosperm at 40° C. with dilute *saliva* for a few hours. In this way the starch-granules are completely dissolved, leaving a beautiful reticulum of protoplasm showing the cavities originally occupied by the starch-granules. On staining with methyl-green or eosine, the nuclei are rendered visible. This method of clearing sections of their starch by means of saliva is a highly convenient one, since it leaves the other cell-contents almost completely unacted upon, which is not the case with the methods ordinarily in use.

The *embryo* is situated laterally at the base of the seed, and, on the side adjacent to the endosperm, has a shield-like expansion of its hypocotyl, the *scutellum*, *scut.*, which is characteristic of the seeds of the Gramineæ, and which, lying as it does in close contact with the endosperm, serves as a special organ of absorption, through which, during germination, the nutritive matter stored in the endosperm must pass on its way to the growing portions of the embryo.

The actual line of separation between the embryo and endosperm is marked by a line of cells forming a well-marked *epithelium*, *t. abs.*, which covers the whole of that portion of the scutellum in contact with the endosperm.

In the case of barley, the cells of this epithelium are very columnar in shape, having a length of about 0·03 to 0·04 mm., and a breadth of 0·01 mm. They are arranged with their longer dimensions normal to the surface of the scutellum, and, whilst the bases of the cells are closely united with the subjacent tissue of the scutellum, their free extremities are in the very closest contact with the depleted layer of cells, *t. am. exs.*, of the endosperm, but are not, except in very rare instances, in any way organically united with this tissue.

We shall have occasion, at some future time, to describe the appearance of this epithelium as it occurs in many of the Grasses. In all cases its individual cells are columnar in form throughout the greater part of the scutellum, and this structure we find assumed at a very early period of its developmental history.

The cell-walls of the epithelium are very thin, and are not in the least cuticularised. The cell-contents, before the commencement of germination, are very finely granular, and the nucleus, which is large and elliptical in shape, lies near the base of the cell with its longer dimension across the cell.

The modifications which the cell-contents undergo during germination will be referred to in detail later on.

Since the whole of the reserve matter of the endosperm must traverse this columnar epithelium on its way to the growing parts, and this special form of cell is absent from the exterior regions of the scutellum, which do not border on the endosperm, it has been concluded by physiologists that its functions must have an intimate relation to this transference of nutritive matter. Sachs first recognised this, and gave the name of *absorptive epithelium* ("Aufsauge-Epithel") to this particular tissue. We shall have occasion to show, later on, that this function of absorption is one which the epithelium shares with the deeper-seated cells of the scutellum and the principal organs of the axis, whilst the properties which markedly differentiate it physiologically from the other tissues are its specialised *secretory* functions.

The cells of the scutellum underlying the epithelium are polyhedral, and have well-marked laminated walls and conspicuous intercellular spaces.

A few words descriptive of the contents of these and of other cells of the embryo will not be out of place, as but very few observations have been made on the subject. If sections are made from the dry embryo of barley tangential to the surface of the scutellum, and these are examined in alcohol, the cell-contents of the scutellar parenchyma are seen to consist principally of minute spherules of *aleurone*, which can be seen, on suitable treatment with reagents, to be embedded in a fine protoplasmic network. The minute globules of fat which are mingled with the aleurone-grains run together, and become much more conspicuous after treating the section with water or alcohol. If the fat is dissolved by means of ether, the spherules of aleurone appear with very great distinctness and in a state very favourable for examination with reagents. They give all the usual microchemical reactions for proteïds, and on flooding the section with water the grains lose their sharp spherical contour, swell up slightly, and exhibit pitted markings on their surface, clearly indicating that a portion of their substance has been dissolved. Continuous washing with water does not completely dissolve the grains, although they are much altered in form by such treatment; but they are completely and *instantaneously* dissolved by a 10 per cent. solution of sodium chloride, with the exception of an extremely minute *globoid* of an inorganic salt, without any crystalline structure, and consisting probably of the double phosphate of calcium and magnesium.

If the sections have been lying in alcohol for any length of time, the aleurone-grains acquire the power of resisting, to a great extent, the action of both water and sodium chloride solutions. As regards the nature of the albuminoïds composing them, it appears pretty certain that these aleurone-grains of the scutellum contain at least two distinct compounds, one belonging to the class of the *albumoses*, the other to that of the vegetable *globulins*. In this respect they resemble the aleurone-grains of most seeds which have been examined.

Immediately below the scutellum, and in intimate organic connection with it, are the main organs of the axis, the *plumule* and *radicle*. The former consists of four rudimentary leaves, $f._1$, $f._2$, $f._3$, $f._4$, enclosed in the plumule-sheath, *ksch.*, whilst the primary radicle, with its root-cap, is completely embedded in the coleorhyza, or root-sheath, *col.* The commencement of secondary radicles can frequently be seen in the mature and resting embryo; these arise in the meristematic portion of the hypo-cotyledonary axis, *x*, lying between the primary root and the plumule.

In the zone of tissue between the bases of the plumule and the radicle some procambium strands, *proc.*, take their rise and can be followed thence into the scutellum, the rudimentary leaves of the plumule, and into the axial fibro-vascular cylinder of the radicle. These procambium strands represent and mark out the future vascular bundles.

The cells of the coleorhyza contain protoplasm which is comparatively clear and ungranulated, and possess a nucleus which becomes very well defined on staining with aniline-green. In a median sagittal[*] section of the embryo, such as that depicted on Plate I, it is seen that, in form, the cells of the coleorhyza do not differ essentially from those of the scutellum, but the difference in the cell-contents is very strongly marked. The meristematic portion, *x*, lying between the bases of the plumule and radicle, is made up of cells containing some fat, and filled with a protoplasm which is decidedly more coarsely granular than that of the coleorhyza cells themselves. As the tissue is traced downwards into the coleorhyza, the cell-contents are seen to become less granular, the passage from one kind of cell to the other being very rapid.

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[*] In order to avoid periphrasis as much as possible, we have adopted the following terminology as being convenient for use in describing the anatomy of the various parts of the seed. The terms have been for the most part borrowed from those in use by human anatomists.

The furrowed side of the grain, *i.e.*, that which is covered by or adjacent to the superior palea, is the *ventral* surface, the opposite side being *dorsal*. The aspect of any part nearer to the embryo is called *proximal*, whilst that more remote is *distal*. A plane or section carried longitudinally through the ventral and dorsal surfaces (that is, from front to back) is called a *sagittal* section, the longitudinal plane or section at right angles to this being *coronal*. The sagittal plane which divides the grain into two symmetrical halves is the *median sagittal* plane. A plane or section carried across the grain, at right angles to the sagittal and coronal planes, is *transverse*, the *median transverse* or *equatorial section* being the one which divides the grain midway between its upper and lower apex.

(3.) *The Visible Changes which occur in the Embryo and Endosperm during Germination.*

The mature and resting embryo either contains no starch at all within its tissue or but the merest traces, which are generally confined to the basal margin or "heel" of the scutellum, but we have also occasionally observed a few starch-granules remaining in the periblem of the radicle, and in the meristematic tissue, *x*, between the plumule and radicle. In the early stage of its development from the oosphere, starch is, however, abundant in the young embryo. When the embryo has so far developed as to have a length of about 2 mm. and a breadth of 1·5 mm., starch is abundantly present in the scutellum, and also, but to a less extent, in the coleorhyza and plumule-sheath. As the embryo acquires its full dimensions, its cells are gradually depleted of their starch, until, as we have seen, but mere traces remain in the mature and resting germ. When, after the resting period, the seed is put under conditions favourable for germination, the first visible signs of growth are accompanied by a *re-appearance of starch* in certain portions of the tissue.

The first indications of growth are afforded by an elongation of the primary radicle, and before this has broken through the coleorhyza, this and the periblem of the radicle itself are found to contain starch abundantly, and this substance can also be detected in the leaves of the plumule. Up to this point the cells of the scutellum still remain free from starch, but their contained aleurone-grains have more or less disappeared, leaving a coarsely granulated protoplasmic matrix containing abundance of fat or oil.

As germination continues, by the time the primary root has broken through its coleorhyza, and the plumule, enveloped in its sheath has ruptured a portion of the opposing integument of the seed, abundance of starch makes its appearance in the plumule-sheath, the periblem of the radicle, the root-cap, and, speaking generally, in all the parenchymatous tissue immediately surrounding the young vascular bundles. This is the so-called starch-conducting tissue of Sachs, which a little later on becomes perfectly gorged with starch. Neither the vascular tissue itself nor the actively growing points, as has been pointed out by Sachs, contain a trace of starch, and it is less abundant in the remains of the coleorhyza than it is at the very commencement of germination. The cells of the *scutellum*, when the primary radicle is just breaking through its sheath, begin to show indications of small starch-granules which are embedded in the protoplasm, and rapidly increase in size and number. Prolonged investigation has shown us that these starch-granules appear first of all in the *cells of the scutellum immediately underlying the absorptive epithelium*, and that they gradually invade the underlying parenchyma. Taking this into consideration, and also the fact that the appearance of starch in the scutellum is coincident with the very earliest signs of a dissolution of the endosperm, we cannot but conclude that we have here the first visible indication of a passage of the reserve material of the endosperm to the actively growing parts.

We have very carefully examined the changes which take place in the *epithelial* cells, more especially since we have recognised their highly important secretory functions. Within a few hours of putting the moistened grain under conditions favourable for germination, we have invariably noticed that the very finely granulated and semi-transparent protoplasm of the epithelial cells *becomes much coarser in structure*, and the granulations, increasing in size and number, so far cloud the contents of the cells that the nucleus, which is such a conspicuous object before this change is brought about, becomes almost invisible. The clouding of the cell-contents appears to reach its maximum in from 24 to 36 hours, or even less, and but little further change in this direction can be noticed until the young plant has grown to a considerable size, and the endosperm is almost exhausted of its reserve material. As this stage is approached, and the epithelium ceases to function as a secretory and absorptive tissue, the cell-contents clear again, and become even more transparent than they were originally. The protoplasm has at this stage almost entirely lost the coarse *granularity* which characterises it in the earlier stages, and now contains but a very few extremely small and highly refractive granules. The cell-contents become almost perfectly hyaline, and afford no indications of a cell-nucleus.

We shall have occasion to refer once more to these well-marked histological changes in the cell-contents of the absorptive epithelium, which are paralleled by somewhat similar changes in certain secretory cells both in animals and vegetables.

As germination proceeds, and the contents of the endosperm are gradually absorbed, the free ends of the epithelial cells become somewhat club-shaped, and, losing to a great extent their lateral adhesion to each other, form a sort of velvety pile, or a collection of minute villi, which project into the endosperm. This change is accompanied by an apparent elongation of the columnar cells.

We must now turn our attention to the visible changes which take place in the *endosperm* itself. The first traces of any action upon its contents are apparent as soon as the primary radicle has burst through the coleorhyza, that is, after 24 to 36 hours' germination. At first the action is wholly confined to a softening and partial dissolution of the cellulose of the depleted layer of cells lying at the proximal end between the absorptive epithelium and the starch-containing cells of the endosperm. This period corresponds to the first appearance of transitory starch in the scutellum, and there cannot be a doubt that the cellulose of the depleted layer is the first portion of the reserve material which is put under contribution for supplies to the budding embryo. Different portions of the depleted layer do not equally resist dissolution, and, as a general rule, we have found that when the upper two-thirds of the layer, as seen in a longitudinal section, have been completely disintegrated and dissolved, the remaining third, adjacent to the ventral side of the grain, still to some extent retains its structure.

The extension of action upon the contents of the endosperm is marked by a dissolution of the walls of the starch-containing cells, and the action proceeds progressively from the proximal to the distal regions of the endosperm. The action upon the starch-granules never takes place *as long as the walls of the cell containing them are intact*. It is true that action upon the starch-granules in the immediate neighbourhood of the scutellum can be detected at a very early stage of germination (we have found very distinct action when the primary radicle was 2 mm. long and the plumule 1½ mm.), but in all these cases the extension of the action upon the cell-walls themselves is far in advance of any visible action on the starch.

The phenomena attending the disappearance of the cell-walls are briefly as follows:—

In the first place the cell-wall swells up slightly, and its stratification becomes much more apparent, owing to a partial separation of its constituent lamellæ. These are gradually disintegrated, but the middle lamella appears to offer a somewhat greater amount of resistance than the others. Ultimately, the whole of the cell-wall is broken down into very minute, spindle-shaped fragments, with their longer dimensions arranged tangential to the original cell-wall. Owing to this arrangement, these minute fragments, when viewed with low powers, give the appearance of a ghost-like cell-wall for some time after the wall has really ceased to be continuous. Ultimately, as the action continues, the residual fragments also disappear, and there is no visible sign of separation between the contents of contiguous cells.

As these changes proceed, the whole contents of the endosperm become considerably softened, and can readily be broken down between the finger and thumb. This is the so-called "mealiness" of

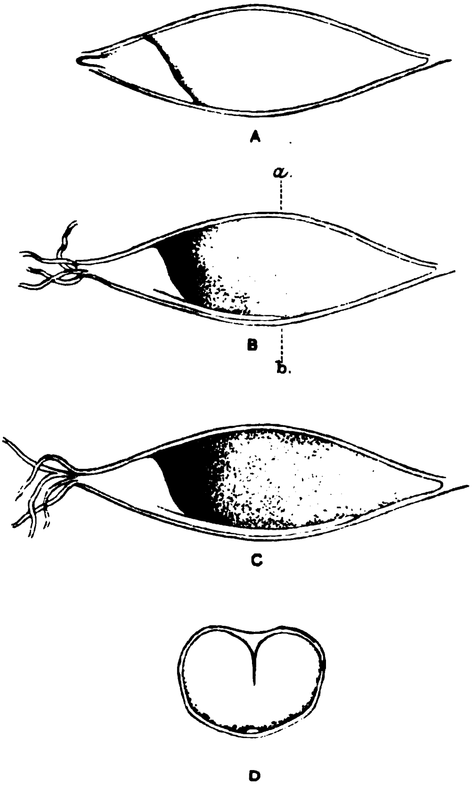

Plate 2

Diagram shewing the progress of the dissolution of the cell-wall of the endosperm of barley at different periods of growth. The advancing disintegration of the contents of the grain is indicated by shading.

A . at 3 days
B „ 6 „
C „ 10 „

D Transverse section of B at a b.

the grain which it is the aim of the maltster to produce to the fullest extent during the limited germination which constitutes the malting process. We find that this production of mealiness in the contents of the endosperm is undoubtedly *co-terminous with the dissolution of the cell-wall*, and, contrary to what is usually believed, is entirely independent of the disintegration of the starch-granule. In other words, the "mealiness" is an accurate macroscopical indication of the progress and extent of the dissolution of the parenchymatous cell-walls. This can be best proved by making a longitudinal section of a partially germinated grain of barley, and excising very minute portions of the endosperm with the fine point of a scalpel at definite distances from the scutellum. The fragments are warmed gently on a glass slide with a fairly strong solution of caustic potash in order to dissolve the starch, and the condition of the cell-walls determined.

The dissolution of the cell-wall takes place in certain definite directions in the germinating grain. Commencing, as we have seen, in the depleted layer of cells in contact with the epithelium of the scutellum, its progress along the grain is considerably more rapid on the dorsal side, immediately under the advancing plumule, than on the ventral.

This phenomenon, which is indicated diagrammatically in Plate 2, is not due to any direct influence exercised by the growing plumule across the endocarp and testa, for it is also observed to just as marked an extent in the Gramineæ in which the plumule* grows entirely outside the integuments of the caryopsis; and, moreover, the same thing is observed when this external growth of the plumule is artificially brought about in ordinary barley. The explanation is to be found in the less resistance of the cell-walls on the dorsal side to the action of the special agent which produces the dissolution. This is no doubt intimately connected with the fact that the cells of the parenchyma on the dorsal side are younger in point of development, and are consequently less likely to have had their cell-walls altered in the direction of lignification.

The walls of the starch-containing cells of various barleys differ materially in their tendency to ready dissolution during germination; in some varieties the resistance is considerable, whilst in others the cellulose yields very readily. This is dependent to a very great extent upon the influence of soil and climate; but, speaking generally, it may be stated that the varieties of barley which are most prized for purposes of malting are those in which the cell-walls give way with the greatest facility.

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* In an early paper by one of us and Heron (Trans., 1879, 35, 623), we stated our belief that the plumule, as well as the scutellum, is distinctly concerned in the absorption of reserve material; this, however, is certainly not the case.

The dissolution of the cell-wall as a first step to the absorption of the reserve materials takes place, doubtless, in the seeds of all the Gramineæ. We have observed a great number of these, especially of the cereals, and have found no exceptions to the rule.

In the case of the horny seeds of the brome grasses, we find the walls of the endosperm cells thickened to such an extent as to constitute a very important part of the reserve material. In *Bromus mollis* and *B. asper* this is the case to a very marked extent, and to a less degree also in *B. sterilis*.

We have germinated the seeds of the first mentioned species, and find that the highly thickened cell-walls gradually thin down, and are completely dissolved within a very short time, thus liberating the small grains of starch and the other contents of the cells. The action extends even to the walls of the aleurone-cells themselves, which, as we shall see presently, are in the seeds of the cereals highly resistant.*

The first visible action upon the *starch* of the endosperm, as in the case of the cellulose, takes place in the *immediate neighbourhood of the scutellum*. The earliest indication of such an action can generally be obtained when the primary radicle of the embryo has acquired a length of about 2 mm., and the plumule about 1·5 mm.

As we have already stated, the dissolution of the cell-wall always precedes the attack upon the starch, and progresses much more rapidly than the latter. Both actions take their course along the same lines in the grain, and Plate 2, which represents the progress of the dissolution of cellulose, represents also that of the dissolution of starch, the latter, however, falling behind the former in point of time.

The extent to which the dissolution of the cell-wall precedes that of the cell-contents is shown by the following observations, which were made upon partly germinated barley placed under the ordinary conditions of malting for a period of five days. Tracing the cells of the endosperm, on the dorsal side, from the scutellum to the apex of the grain, it was seen that all traces of cell-walls had disappeared for a distance of 3 mm. from the scutellum, that is, for about one-third of the length of the grain, and partial action upon the cell-walls could be traced for about 1·5 to 2 mm. further; beyond this point the cell-walls were untouched. On the other hand, indications of action upon the starch-granules did not extend in a distal direction for more than 0·15 mm. from the scutellum.*

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* That the dissolution of the cell-wall invariably *precedes* that of the cell contents during the breaking down of the endosperm is a fact of the highest physiological importance, and one which for the most part has been strangely overlooked. We have been able to discover only two allusions to it in the writings of previous observers. The one is by Lermer, in 1868 (*Dingl. polyt. Journ.*, **188**, 324), the other by Frankhauser in 1886 (*Der Bund*, **37**, No. 26. Berne). Further reference will be found later on to the work of Frankhauser.

The phenomena which the starch-granules themselves exhibit during dissolution have been described by so many observers that it is unnecessary to say much on this point. In the case of germinating barley, minute pittings on the surface of the granules are the first indications observed of any action on the starch. These pittings increase in number and depth until the granule has assumed a very irregular outline, and at a later period the occurrence of radial clefts and a tendency for the laminæ to separate from each other result in a constantly increasing surface being exposed, and the speedy and complete dissolution of the granule. Some of the concentric laminations of which the granule is made up resist dissolution much more than others, and often survive for a considerable time as the so-called "starch-skeletons."

Although this mode of dissolution of the starch-granule is the one which is ordinarily observed during the breaking down of an endosperm in germination, it is essentially different from the phenomena observed during the dissolution of transitory starch in an intact and *still-living cell*, when the tissue of which the starch-containing cell forms a part is put under contribution to supply material to another growing part of the plant. As we have found that the seeds of the Grasses illustrate these two different modes of the dissolution of starch in a very striking manner, we must refer to them somewhat in detail.

We have already referred to the fact that the development of the embryo within the embryo-sac is much later in point of time than the development of the endosperm, and that the embryo increases at the expense of the tissue of the previously formed endosperm, which it invades and to some extent absorbs. The cells of the endosperm which are so absorbed contain, in their original state, large and fully formed starch-granules, not differing in their appearance from those of the mature grain, and it might be expected that their dissolution and disappearance would take place much in the same manner as that observed after the resting period is over and germination has commenced. Such, however, is not the case, for we have found, after a careful study of the developmental history of the embryo, that the starch-grains of the depleted portion of the endosperm, instead of becoming pitted, fissured, and corroded, as they do during germination, undergo dissolution *from the outside only*, and gradually diminish in size, whilst retaining almost to the last their discoidal shape and translucency.*

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* The preparation of sections from partially germinated grain presents certain difficulties, owing to their want of coherence after the dissolution of the cell-walls. In this and similar experiments, the grain was first hardened with alcohol, glycerine added, and the mixture allowed to remain exposed to the air until the alcohol had disappeared, leaving the tissue perfectly saturated with glycerine, and fairly coherent. This method is described by Bower and Vines in their "Practical Instructions in Botany."

As the starch and protoplasm are absorbed, the shrinkage of the cell-contents is accompanied by a compression of the cell-walls between the scutellum of the advancing embryo and the unaltered tissue of the endosperm, with a corresponding diminution in the capacity of the cells.

Although a superficial examination of the phenomena might lead to the belief that the physiological functions of the embryo during *germination* are but an extension, after a resting period, of those exercised during its *development*, it is clear that this can at any rate only be true to a limited extent.

Whilst in both cases we have partial dissolution of the endosperm, and assimilation of its substance, we must notice the following important points of difference:—

During *development* of the embryo, the *cell-walls* of that portion of the endosperm which is absorbed remain intact and the starch-granules are dissolved symmetrically and without corrosion; whilst, on the other hand, during *germination*, the cell-walls of the endosperm are most readily attacked, and the starch-granules are dissolved after very irregular pitting and corrosion. This difference in behaviour of the starch-granules is not due to any intrinsic difference in the nature of the granules at the two periods, for we have found that the partially-formed granules from the immature and developing endosperm, like those from the mature grain, are capable of being dissolved by pitting and corrosion, when they are acted upon by a solution of prepared diastase. Some light will be thrown upon the cause of these differences in a later part of this paper.

We have now only to consider the visible changes which are effected during germination in the aleurone-cells, which form the peripheral layer of the endosperm. These cells, whilst differing very much in the various Grasses in size, shape, and number of layers, agree in all cases in possessing very thick and more or less cuticularised cell-walls, and cell-contents consisting of spherical aleurone-grains and a certain proportion of fat or oil.†

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* When almost on the point of disappearing, the starch-granules do become a little irregular in outline and somewhat less translucent, but nothing like pitting or corrosion can be at any time detected.

† Tangl showed in 1885 that the fat-containing cells (aleurone-cells) of the seeds of Grasses have in their cell-walls minute perforations which establish a continuity of protoplasm from cell to cell. He had previously shown, in 1879, a similar continuity of protoplasm in the endosperm cells of certain other seeds.

Careful observation upon germinating barley has convinced us that neither the walls of the aleurone-cells, nor their contents, are visibly altered during the early stages of growth, corresponding to the malting period. It is only when the plumule projects about 4 or 5 mm. from the apex of the grain that any signs of alteration can be observed; the aleurone-grains then lose their sharp spherical contour, becoming somewhat uneven in outline, and the cell-walls, which, in their unaltered state, are very transparent, begin to show signs of lamination. We are by no means convinced, however, that the alteration in the appearance of the aleurone-grains at this stage is due to any direct influence of germination, since the grains undergo a similar alteration in water only, providing this is afforded free access by dividing the cuticularised cell-wall.

When the endosperm is nearly exhausted of its reserve starch, and the young plant has acquired a length of about 100 mm., the walls of some of the aleurone-cells show very strong signs of dissolution, and, even where still continuous, exhibit a very marked stratification, a phenomenon which we invariably find preceding dissolution. Where complete or partial dissolution of the cell-wall has taken place, the cell-contents are also very much acted upon; but it is not difficult to find, even at this stage of germination, some aleurone-cells which scarcely exhibit any change in appearance.

In the case of barley, and of the cereals generally, there can be no doubt that the aleurone-cells contain a store of proteïd reserve material which is destined only for the *late use* of the plant, and that this is conditioned by the highly resistant properties of the containing cell-wall.*

It has been suggested at various times that the cells of the aleurone-layer of the endosperm exercise an important influence on the dissolution of starch during germination, either by a direct excretion of diastase, or, as suggested by Tangl, by acting as a conductor of diastase from the embryo. Our experiments, so far, are opposed to this view; but we hope at a future time to enter fully into this important question (see Addendum, p. 520).

In the germination of *Bromus mollis* the dissolution of the aleurone-cells, by a gradual process of thinning down, goes on much more rapidly than in the case of barley, considerable action taking place within five or six days of the commencement of germination. This is due, as will be shown in a future communication, to the much greater activity of the particular cellulose-dissolving agent in this species of Grass.

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* In a remarkable series of physiological experiments carried out upon himself by Aimé Girard (*Ann. Chim.* [6], 3, 289) in order to determine the alimentary value of the proteïds contained in the outer (aleurone) layers of the endosperm of wheat, he showed that the aleurone-grains passed through the alimentary canal apparently unaltered. The protection of the proteïds against the action of the digestive secretions is doubtless entirely due to the highly impermeable nature of their cell-walls.

(4.) *The Relation of the Embryo to the Endosperm that of a Parasite to its Host.*

From the ease with which the embryo can, with due precautions, be separated from the endosperm without the rupture of the tissue of either, it is evident that the relation of the two is merely one of very close apposition.* In most of the Gramineæ there is no trace of any organic connection between the essential parts of the seed, and a study of the developmental history of the embryo within the embryo-sac confirms this. After the disappearance of the *suspensor* and the incorporation of the *hypophysis* with the root-cap, the embryo is free in the apical portion of the sac, and for its further development is dependent upon the young endosperm.

It is to Sachs that we owe the recognition of the exclusively parasitic nature of the embryos of normal plants, while the endosperm is still unexhausted of reserve materials, and before the appearance of chlorophyll in their tissue. Just as most of the phanerogamous parasites are connected with their host-plant by means of special *haustoria*, through which the substances of the host must pass into the parasite, so, in the case of the Grasses, we find a part of the axis, the *scutellum*, specially modified so as to function as a haustorium, through which the altered reserve materials of the host-like endosperm pass, on their way to the growing part of the young plant.

In one particular, however, as Sachs has pointed out, the scutellum differs from the haustorium of ordinary parasites; the absorbing organ of the seedling is not organically connected with the endosperm, but is only in close contact with it, whereas "the haustoria of parasites become so intimately connected with their host-plants, that it is often difficult to decide where the boundary between the two lies." ("Physiology of Plants," p. 373.)†

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* The only exception we have found to this is in the case of maize, where there is to some extent a continuity of tissue between the epithelium of the embryo and the cellular tissue of the endosperm. This continuity of tissue which is, however, very incomplete, accounts for the difficulty experienced in dissecting out the embryo of maize in its entirety. As soon as germination has commenced, the connecting tissue disappears, and the embryo can without difficulty be separated from the endosperm.

† Some doubt has of late been thrown upon the generally received statement that the embryo, during germination, derives its nourishment from the endosperm only through the intermediary tissue of the scutellum. Matthews and Lott, in their recent work on "The Microscope in the Brewery," p. 148, suggest that the

Granting the parasitical relation of the embryo to its endosperm, it appeared to us that it ought to be possible, after dissection of the embryo from its natural host, to cultivate it upon artificial endosperms of known and perfectly definite composition, and in this way obtain information of the highest value in determining the nature of the complex chemical changes attending germination.

The results of some preliminary experiments in this direction were described by one of us towards the close of the year 1888 (see Presidential Address for 1888, *Transactions of Burton-on-Trent Natural History Society*, **1**, 110). At that time we were under the impression that no attempts had been previously made in this direction, but careful search has shown us that a few workers have carried out experiments upon the artificial nourishment of the excised embryo of certain seeds, but, for the most part, they have had in view a different object from the one which we have referred to above. It will be necessary, in the first place, to give a short account of the work of these observers.

In an important memoir on germination, published by A. Gris, in 1864 (*Annales des Sciences Naturelles, Botanique* [5], **2**), the author, whilst describing the distribution of transitory starch in the embryos

aleurone-cells, which are, on the one hand, in contact with the starch-containing cells of the endosperm, and on the other with the germ, may function in some way as *conductors* of nutriment from the former to the latter. That there should be any direct transference of reserve material from the starch-containing cells of the endosperm across the walls of the aleurone-cells seems improbable, since the walls of the latter are thick and highly cuticularised, a condition very unfavourable to the ready transmission of even highly diffusible substances.

Since, however, it has been shown by Tangl that there is a continuity of the protoplasm of these cells through minute perforations in their walls, it did not seem altogether impossible that they might possess some such function as that suggested by Matthews and Lott. The following direct experiments were consequently made with a view to solving the question.

After softening barley in water, the paleæ were removed from the base of the grain and the fine point of a scalpel was then passed completely round the edge of the scutellum at its junction with the endosperm. In this way the continuity of the aleurone-layer was broken, and manifestly nothing could pass along these cells from the endosperm to the embryo. The operation is a little difficult to carry out, as of course all the retaining integuments are severed, and great care has to be taken not to displace the embryo. It was found that the corns so treated germinated as freely, and produced plants which were as healthy and vigorous as those derived from the unmutilated grain, facts which are not consistent with the view that the aleurone-layer plays an important part as a conductor of reserve material from the endosperm to the embryo.

The experiment is also equally against Tangl's view that the aleurone-layer functions as a conductor of diastase from the embryo to the principal mass of the endosperm cells, since the breaking down of the starchy contents of the endosperm occurred to the same extent in both cases.

of seeds, incidentally mentions the fact that he had succeeded in germinating the excised embryos of *Mirabilis jalapa* in moist sponge.

Van Tieghem, in 1873, in a paper entitled "Recherches Physiologiques sur la Germination" (*Annales des Sciences Nat.* [5], **17**, 205), discusses (1) the question of the mutual dependence of the various parts of the different organs of the embryo, and (2) the degree of dependence of the entire embryo upon its "*albumen*" (endosperm).

In order to arrive at conclusions upon the first of these points, he effected systematic mutilations of the embryo before germination. Taking the seeds of *Helianthus annuus* as a type of ex-albuminous seeds; he dissected out the radicles, plumules, and cotyledons, and found, to a certain extent, that the separated portions were capable of independent growth, and that in some cases there was even a regeneration of some of the organs. Thus, for instance, the plumule occasionally regenerates radicles at its base, whilst the cotyledons develop chlorophyll within their tissue, and produce after some days several adventitious roots, and even perfect plants. It was also found that a fragment of any organ of the embryo germinates independently of any other fragment. These fragments develop as though they still formed part of the particular organ from which they were derived, and proportionately to the amount of nutritive assimilable matter which they contain at the moment of separation.

The experiments upon "*albuminous*" seeds were conducted upon *Mirabilis jalapa* and *Zea Mays.* Here again the independent reproduction of various parts of the embryo was found to take place, but the *scutellum* itself has no such power.

The portion of Van Tieghem's work which has the most direct bearing on our enquiry is, however, that dealing with the degree of dependence of the embryo on the endosperm. In *Mirabilis jalapa* it was found, when the embryo was separated from the endosperm and germinated alone, that for a few days its development was comparable with that of embryos still attached to their endosperm, but that this equality of growth was maintained but for a comparatively short time, the development in the former case speedily ceasing.

Attempts were then made to ascertain if it is indispensable that the nutritive material of the endosperm should be contained in the cells of a tissue, and for this purpose artificial endosperms were prepared by triturating the "albumen" of the seed under experiment, making it into a paste, rolling it into little balls, and applying these closely to the embryo.

Under these conditions a sensible absorption of the "albumen" takes place, sufficient to show that the nutritive power of the endosperm is not necessarily dependent upon cellular organization. Similar experiments carried out with artificial endosperms made of potato-starch, potato-starch with phosphates and nitrates, and with the flour of *Polygonum Fagopyrum*, led Van Tieghem to the following generalisation of results. The embryo of *Mirabilis jalapa* (doubtless there are also many other plants which would behave in the same way) can develop into a young green plant without the aid of the "albumen." The influence of the albumen is only manifested at a later stage.

The nutritive matter of the "albumen" can be replaced up to a certain point by a paste formed of its own substance, or by a paste containing the predominating substance of "albumen," *starch*, the nutritive effect of which is increased by the addition of mineral nitrates and phosphates.

In the year 1876 Blociszweski (*Landwirthsch. Jahrbücher von v. Nathusius & Thiel*, 5, 145; and also *Jahrsber. d. Agricultur Chem.*, 1875—6, 232) described a number of experiments which he had made on several kinds of seeds, including those of maize, clover, oat, rye, pea, and lupin. He endeavoured to grow in moist earth the embryos of these seeds separated wholly or in part from their endosperms, or cotyledons, as the case might be. The results indicated that the naked embryo can grow without the aid of the stored-up reserve material of the cotyledon or endosperm, and that assimilation begins provided the plumule has the necessary amount of light. The development of the naked embryo is better the larger the proportion this bears to the total weight of the seed.

These experiments of Blociszweski are, as he himself points out, opposed to those conducted by Sachs with the kidney-bean and maize (*Botan. Zeit.*, 1862, 148), in which the embryo under the most favourable circumstances developed dwarfed plants, and ultimately perished.

Blociszweski also repeated the experiments of Van Tieghem, already alluded to. He supplied the embryos of rye and of peas with artificial endosperms made of (1) the macerated "albumen" or cotyledon, (2) starch, (3) grape-sugar, and (4) asparagin, or with mixtures of these substances. Rye embryos can absorb their own macerated endosperm, starch, and grape-sugar, but not asparagin. The embryo of the pea can make use of starch, sugar, and also of asparagin in very weak solutions, but it cannot absorb nutriment from its own cotyledons after these have been macerated.

The above are, as far as we have been able to ascertain, the only experiments which have any direct bearing upon the germination of the isolated embryos of seeds, and it will be noticed that these have been undertaken more with the object of ascertaining the degree of mutual dependence of the various parts of the embryo, and the amount of dependence of the latter upon its cotyledon or endosperm, than with a view to explain any of the physiological processes attending germination.

The following experiments illustrate in a very striking manner the parasitic nature of the embryo of the seeds of the Grasses.

(5.) *Development of Excised Embryos upon Foreign Endosperms.*

If the inferior palea of a grain of barley softened in water is divided at its base by two or three longitudinal cuts, and the strips are turned back, the outline of the embryo is clearly visible beneath the thin covering of the pericarp and the testa. By passing the sharp point of a small scalpel round the edge of the scutellum the embryo can be removed intact. If a well selected embryo from another grain of barley is now excised, it may, without difficulty, be placed in the position of the first embryo, and, providing the selection with regard to size and shape has been a judicious one, very close adhesion can be brought about between the embryo and its new endosperm. The small flaps of the palea are brought back into their natural position, and, if necessary, a loop of thin silver or platinum wire is passed around the base of the grain to secure the embryo in its place.

When the grain after such treatment is put under conditions favourable for germination, the "grafted" embryo develops into a young plant almost as readily as if it were still dependent upon its own endosperm. The contents of the foreign endosperm undergo all the usual changes attending their absorption, and, in fact, if we have been fortunate enough to exclude the germs of mould during the operation, the growth is in every way normal.

We have succeeded also in obtaining a partial development of the embryo of barley upon the endosperm of *wheat*, but the growth of the barley plant is not very perfect under these conditions, owing to the great difference in size and shape between the wheat and barley embryo, and the consequent difficulty of adjustment in such a manner as to provide sufficient contact to ensure rapid absorption.

(6.) *The Starch-containing Portion of the Endosperm to be regarded as a Storehouse of Dead Reserve Material, no Residue of Vitality being recognisable in its Cells.*

It is of the highest importance to determine if, in the ripe and resting seeds of the Grasses, vitality is confined to the embryo, or if, on the other hand, there is any residual life in the cells of the endosperm; for on the answer to this question depends the degree of complexity of the problem before us, that is, an elucidation of the chemical changes occurring in the reserve materials of the endosperm during germination.

It is clear that if the endosperm can be shown to be a reservoir of material stored in cells which have lost all those functions which we associate with the word *vital*, the problem will resolve itself into a study of the chemical changes brought about in dead inert material, and initiated in some way or other from without, through the agency of the embryo. If, on the other hand, the cells of the endosperm retain, in the same way as do the cells of the embryo, any of the vitality which they undoubtedly possessed during development, and as long as reserve material was being deposited within them, then the chemical processes expressing the changes brought about by the metabolic activity of those cells may be in the highest degree complicated and difficult to follow.

Hitherto but few experiments have been made with the special object of determining if the endosperm of seeds retains any vitality, and does anything towards preparing its contained reserve materials for the embryo; and, as far as we have been able to ascertain, no direct experiments of the kind have been made on the seeds of the Grasses.

A. Gris found (*Annales des Sciences Nat.*, *Botanique* [5], **2**, 5, 1865) in the case of *Ricinus communis* that, after complete absorption of the cell-contents of the endosperm under the influence of germination, there is developed in some of the cells a rose-coloured substance, whilst others show a protoplasmic layer and a nucleus around which very small starch-granules are in course of development.

In 1877, the subject was more fully examined by Van Tieghem (*Compt. rend.*, **84**, 578), who found that the endosperm of *Ricinus* when separated from its cotyledons, showed unmistakable signs of development when placed under favourable conditions, such internal changes taking place in its tissues as to prove beyond all doubt that the cells composing it are still living. No such changes, on the other hand, could be induced in the following seeds after they were deprived of their embryos: *Mirabilis longiflorus*, *Canna aurantiaca*, *Aucuba Japonica*, and *Phœnix dactylifera*.

The general conclusions at which Van Tieghem arrives are that an endosperm, such as that of *Ricinus*, containing oil and aleurone as reserve materials, is endowed with a vital activity of its own, by virtue of which it digests the reserve material, which has then only to be absorbed by the embryo. On the other hand, the endosperm of seeds whose reserve materials consist of starch and cellulose remains passive during germination, and the digestion of its reserve materials is in this case effected by the embryo.*

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* J. R. Green, in a recent paper on the "Germination of *Ricinus communis*,"

In the case of barley, we have never been able to detect in the starch-containing cells of the endosperm any histological changes at all suggesting residual vitality in the remnant of the protoplasm enclosing the starch-granules, and the readiness with which, in the very early stages of germination, these cells are completely broken down and disintegrated tends to negative the idea that the protoplasm is still living. From the highly nucleated state of the aleurone-cells, on the other hand, and from the general tendency of the observations of Van Tieghem, just alluded to, there does seem a considerable amount of probability that these peripheral cells of the endosperm may still retain some vitality throughout the resting period of the seed. This is a question which will, however, require separate treatment, and it must be understood that the following observations refer only to the principal mass of the endosperm—the starch-containing cells.

It is manifest that the proof of the non-existence of vitality in these cells must, like all negative propositions, be a matter of considerable difficulty; the probability of the supposition being correct will, however, be increased if it can be shown that the cells of the endosperm when put under apparently most favourable conditions cannot originate any change within themselves, and it will be rendered still more probable, and the whole idea of residual vitality shown to be superfluous, if an endosperm has been treated in such a manner as to destroy with certainty any residual life which it might contain, and a living embryo grafted upon this endosperm is found to produce in it all the changes incident to normal germination.

We have already considered the physical changes which take place in the endosperm when the intact seed is placed under conditions favourable to germination, but the changes are of a totally different nature if the embryo is previously excised. Under these altered conditions, no change is observable in the endosperm which cannot be directly attributed to the action of micro-organisms from without; on the one hand, from the penetration into the tissue of the mycelia of fungi, and, on the other, from the attack of Schizomycetes of various species, which gradually pulp and disintegrate the mass of tissue from without inwards.

It is manifest, however, that the fact of no visible changes taking place in the endosperm under these conditions is no proof of an absence of metabolic activity in the parenchymatous cells, since no provision is made for the removal of the products of metabolism, a removal which is brought about under natural conditions by the "centripetal" action of the growing embryo.

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communicated to the Royal Society, January 31, 1 90, fully confirms Van Tieghem's statement as to the vitality of the endosperm of the seed of that plant.

In order to meet this objection, a number of grains of barley, with their embryos removed, were arranged with their proximal ends inserted in small holes in a mica plate, which was suspended at the surface of water in such a manner that the endosperms were immersed for a distance of a few millimeters. By this arrangement, any products of metabolism could readily diffuse through the "depleted layer." The experiment was varied by using water, and extremely dilute formic or hydrochloric acid,* but in no case could the slightest indication be obtained of any physical or chemical changes arising within the cells of the endosperm under these conditions, even after the lapse of a considerable time. The tissue was, however, slowly invaded from without by Schizomycetes, especially *Bacillus amylobacter*, which gradually separated, and ultimately destroyed, the walls of the starch-containing cells.

In the second series of experiments, living embryos were "grafted" upon endosperms which had been treated in such a way as to destroy any residual life in their cells. In the first instance, we submitted dry barley to the action of chloroform vapour for 24 hours. The grain was then heated for four hours to 90—100° C., and, after soaking in water, the dead embryos were removed and replaced by those obtained from fresh barley. The embryos so treated readily grew into perfect plants, and this growth was accompanied in the endosperms by all the usual physical changes which occur under natural conditions of germination. Striking as these results are, they were not deemed conclusive, since it was not certain that the chloroform had sufficiently penetrated the grain, or that the application of dry heat had been sufficiently prolonged to destroy all traces of vitality which the endosperm cells might retain. The experiment was consequently repeated, using the endosperms of barley which had been softened in water, and then *immersed in strong alcohol for about six months.* After drying off the greater part of the alcohol at a moderate temperature, the grain was heated for some time in the air-bath at 90—100°, and then steeped in water for 48 hours, changing the water frequently in order to remove all trace of alcohol. After excising the dead germs, living embryos were grafted upon these corns; they grew perfectly, and produced in the endosperms all the ordinary visible changes which accompany normal germination.

The whole of these experiments are against the view that the changes observed in the endosperm during germination are in any way dependent upon its residual vitality, and distinctly favour the view that the *endosperm* of the Grasses is a *dead* store-house of reserve material. Under these circumstances the life of the embryo during the germinating period is strictly speaking not parasitic but *saprophytic.*

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* It seemed to us possible that the endosperm cells might contain a *zymogen* capable of being converted into an active ferment by dilute acid, the existence of proteo-hydrolytic zymogens in some seeds having been proved by J. R. Green.

(7.) *Culture of Excised Embryos of Barley on Water.*

When placed on a moist surface and submitted to a temperature of about 15°C., the excised embryos of barley exhibit signs of growth within a very few hours. The plumule rapidly elongates, and acquires its maximum length in about five days, when it measures from 6 to 8 mm.; its tissue, which at the commencement of growth is fairly turgid, becoming in the later stages extremely flaccid. Simultaneously with the first signs of growth in the plumule, there is a slight elongation of the primary radicle, sufficient in most cases to cause it to break through the coleorhyza, and rudiments of lateral roots also appear, but the total development of the root organs generally is extremely small under these conditions. A considerable loss of dry weight, amounting to about 40 per cent., occurs during an exhaustive water-culture such as we have described, 50 embryos with a dry weight of 0·089 gram weighing only 0·052 gram after water-culture.

Within 24 hours of the commencement of a water-culture, *starch*, which we have already seen is almost entirely absent from the embryo of the resting seed, once more makes its appearance in abundance in certain parts.* It is plentiful in the older cells of the root-caps of both primary and secondary roots, in the periblem of the root, and also in the meristematic tissue *x*, Plate I (p. 460), lying between the bases of the plumule and primary radicle. It is also present in the plumule-sheath, in the "starch-conducting" parenchymatous layers surrounding the young fibro-vascular bundles, and, to a less extent, in the coleorhyza. It will be noticed that the distribution of starch in the embryo during the early period of water-culture is exactly similar to that observed in the very earliest stages of growth when the embryo is still in contact with its endosperm, and before it receives any nutriment from the reserve materials of the latter. In the case of a water-culture however, no starch can ever be found in the aleurone-containing cells of the scutellum, the trifling amount of starch which does arise in this organ being confined to the immediate neighbourhood of the branch of the young vascular bundle which enters it.

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* Vines, in his "Physiology of Plants," p. 217, mentions, as an observation made by Just, that although the embryo of wheat contains no trace of starch when the seed is quiescent, yet, when kept moist for 24 hours, it contains an abundance of starch, although the endosperm has undergone no change. The conclusion is drawn that the starch is formed by dissociation from the protoplasm in the cells of the embryo.

We have already seen that the protoplasm of these aleurone-cells of the scutellum is capable of producing starch in large quantities during the passage of the absorbed endosperm materials, and it is difficult to understand why the transference of the contents of the scutellum cells themselves should not be accompanied by a similar phenomenon, unless we assume that the aleurone, which for the most part makes up the cell-contents, is not capable of being transformed into starch by the metabolic activity of the cell-protoplasm.

That this assumption is probably correct follows from what we know of the chemical nature of the aleurone-grains, and from the fact that the main axial organs, the plumule and radicle, when removed from the scutellum, develop under water-culture almost to the same extent as if the scutellum were still attached, and produce starch within their tissues just as freely. It is consequently highly probable that the reserve materials which are stored within the embryo itself, and which in the early stages afford the mother-substance for the starch of the starch-conducting tissues, reside in the coleorhyza and the meristematic tissue (*x*, Plate I), lying between the bases of the plumule and radicle, the aleurone of the scutellum supplying for the most part only the necessary nitrogenous food.

The amount of starch existent at any one time in the tissues of an embryo undergoing water-culture soon attains a maximum and then rapidly diminishes in amount. At the end of five or six days, when growth has ceased, the starch has once more entirely disappeared, having been used up in conjunction with the other cell-contents in the formation of new tissue.

(8.) *Cultivation of Excised Embryos of Barley upon Nutrient Solutions.*

In ascertaining the nutrient value of a substance, the mode of experiment usually adopted was to place the excised embryo, scutellum downwards, upon a suitable porous medium kept moist with a solution of the nutrient substance under experiment.

In our earlier cultures we made use of discs of plaster of Paris, or of unglazed earthenware, which were partially immersed in the solutions, but latterly we have preferred to use glass-wool, or solutions to which 5 per cent. gelatin had been added. Moistened filter-paper is not to be recommended, since the root-hairs adhere to it with great tenacity, and the paper itself, as will be shown later on, is slightly attacked by the growing embryo. The gelatin mixture has many advantages which render it a highly suitable medium for some cultures, and since the gelatin itself is not assimilable by the young plant, it may be substituted for water in all cases.

In order to avoid the complications which arise under the stimulating action of light, our experiments, unless specially stated to the contrary, were all conducted in the dark, the temperature varying between 15° and 17° C.

When excised embryos which have been entirely deprived of starch by an exhaustive water-culture of five or six days, as described above, are placed upon dilute solutions of certain carbohydrates, such as cane-sugar, dextrose, maltose, &c., starch rapidly makes its appearance in the scutellum, being first visible in the layers of cells immediately underlying the absorptive epithelium. The more remote cells of the scutellum then become filled with starch, which gradually extends to the main axial organs, and invades the parenchyma of the usual starch-conducting tissue. Coincident with this apparent transference of starch *growth recommences.*

The phenomena observed in such a case are exactly similar to those observed during the germination of an embryo attached to its endosperm, but, although a considerable growth may be obtained in this manner if the carbohydrate is one which is capable of ready assimilation, the amount of growth is necessarily limited by the comparatively small quantity of nitrogenous material available for the use of the young plant, which ultimately perishes of nitrogen hunger. There is, however, a sufficient store of proteïds in the scutellum and main axial organs of a freshly excised embryo to allow of a very considerable amount of growth and increase of weight, providing an excess of suitable carbohydrate is also present.

Before considering the relative nutrient value of the substances we have employed in these experiments, it will be well to show the comparatively rapid increase in weight acquired by young plants grown on a solution of a carbohydrate, and to compare the results with those obtained, on the one hand, by culture on the natural endosperm, and on the other, in the water only.

	Gram.
Dry weight of 50 embryos before germination	0·0816
Dry weight of 50 embryos after five days' *water-culture*	0·0490
Dry weight of 50 embryos after five days' growth on natural endosperm....	0·1373
Dry weight of 50 embryos after five days' growth on 2 per cent. cane-sugar	0·1312

Cane-sugar.—Of all the carbohydrates we have examined, this has the highest nutritive value. Abundance of starch is at once found in the tissue of the young plant, and whilst the plumule elongates vigorously the radicles are also well developed, although not to the same extent as when growing on the natural endosperm. This comparatively small development of the roots is characteristic of all artificial cultivations made with carbohydrates only, and is doubtless due to the absence of a sufficiency of nitrogenous food material.

During cultivation of from six to eight days in the dark, we have found that the total increase in dry weight is from three to four times that observed in a pure water-culture. If the plantlets are grown in the light, and the cane-sugar solution is mixed with one of the ordinary mineral nutrient solutions containing potassium nitrate, chlorophyll is produced in the leaves, assimilation commences, and, with due precautions, perfect plants can be reared.

We have made a very large number of cultivation experiments on cane-sugar with a view to determine the concentration of solution most favouring the growth of the embryo. The following experiments show the results obtained by growing 50 embryos on solutions of varying strength for nine days at 15—16°. The total dry weight of the ungerminated and germinated embryos is given, and the average length of the plumules in each case. It will be noted that the length of the plumule decreases somewhat as the assimilation of carbohydrate increases.

Dry weight of 50 embryos before germination 0·082 gram.

Concentration of cane-sugar solution (grams per 100 c.c.).	Average length of plumules in millimeters.	Dry weight after cultivation for nine days.
1·5	28·7	0·143 gram.
2·0	26·7	0·143 „
2 5	27·6	0·191 „
3·0	24·6	0·214 „
3·5	22·0	0·234 „
4·0	22·4	0·236 „

In employing concentrations above 4 per cent., we have always observed a great falling off in the rate of assimilation of the sugar, the optimum concentration being from 3·5 to 4 per cent.

Invert-sugar.—The rate of development of excised embryos in invert-sugar is somewhat less than that observed in the case of cane-sugar under similar conditions.

Dextrose.—The embryos thrive well on solutions of dextrose, but this sugar falls distinctly short of cane-sugar in nutritive value. The optimum concentration is from 3 to 3·5 per cent.

Levulose.—We have experimented with solutions varying in concentration from 1·5 to 4 per cent. of the sugar. The inferior nutrient value of levulose as compared with cane-sugar is very marked. The gain of dry weight of the plantlets is about equal to that observed in dextrose solutions of equal concentration.

Maltose.—This carbohydrate is readily absorbed by the young plant, abundance of starch being produced in the tissues, and active growth taking place. Comparative experiments made with cane-sugar and dextrose indicated that its nutrient value is about equal to that of the latter substance. The optimum concentration of the solution corresponds to about 3·0 to 3·5 per cent.

Galactose.—This compound, one of the products of the hydrolysis of milk-sugar, is capable, in very dilute solutions, of contributing to some extent to the growth of the young plants. We have experimented with solutions up to 4 per cent., and find that whilst a somewhat feeble growth takes place when the concentration does not exceed 1·5 per cent., in solutions of 2 and 2·5 per cent. the growth scarcely exceeds that of a water-culture, and concentrations above this almost completely inhibit growth. Here again, as is always the case in all such experiments where the carbohydrate is not able to contribute to the growth of the plant, the appearance and subsequent disappearance of starch in the tissue takes place exactly in the same manner as in culture on pure water.

Milk-sugar.—In solutions of from 1·5 to 2·5 per cent., the development of the excised embryos progresses for four or five days to the same extent as it would were the plants grown on water only, higher degrees of concentration being actually prejudicial to the life of the plant. If, however, the period of cultivation is extended to nine or ten days, a further slight development takes place, but, from the fact that this is coincident with the appearance of bacterial life and signs of fermentation, we cannot but attribute the recommencement of growth to the products of hydrolysis or of fermentation. Milk-sugar as such cannot contribute to the growth of the plant.

Raffinose.—Since raffinose has been shown by O'Sullivan (Trans., 1886, **49**, 70) to be present in small quantities in ungerminated barley, it seemed extremely probable that it would be found capable of being assimilated by the embryo, and such in fact is the case. When grown on solutions of raffinose of about 2·5 per cent., abundance of starch is formed in the scutellum and in the usual starch-conducting tissues, and there is some development of the plumule, but very little of the roots. The nutrient value of raffinose falls far short of that of cane-sugar, dextrose, levulose, or maltose.

Mannitol.—Mannitol, even in dilute solutions, is incapable of contributing to the growth of the embryo. In a solution of about 1·5 per cent. the plants behave exactly as in water-cultures, but a solution more highly concentrated inhibits growth completely. We have never been able to obtain any evidence of starch-production in the tissues under the action of mannitol; it is absolutely without value as a nutritive material.

Glycerol.—As glycerol is likely to occur in germinating seeds containing fats, it seemed desirable to determine if it is capable of affording cell-forming material to the young plant. A direct comparison of 2 per cent. solutions of glycerol, maltose, and cane-sugar proved that whilst in the glycerol solution a considerable amount of growth takes place accompanied with starch-production, the development is much less than in either of the carbohydrates named.

The following table gives the results of cultivating excised embryos of barley on artificial nutrient solutions under identical conditions:—

Concentration of the solutions, 3·5 grams per 100 c.c.
Period of germination 7 days.
50 embryos germinated in each case.
Plantlets all dried at 100° C.

	Gram.
Weight of 50 embryos before germination	0·0890
,, ,, in water culture	0·0520
,, ,, on natural endosperms*	0·4362
,, ,, cane-sugar	0·1955
,, ,, dextrose	0·1645
,, ,, levulose	0·1625
,, ,, maltose	0·1550
,, ,, invert-sugar	0·1325
,, ,, milk-sugar	0·0990
,, ,, raffinose	0·0910
,, ,, mannitol	0·0895

In all our experiments upon the culture of excised barley embryos on nutrient liquids, there was an evident correlation of visible growth with the appearance of transitory starch in the parenchyma of the scutellum; in fact it could always be determined after the lapse of a short time whether any particular substance was able to contribute to the growth of the young plant, by noting the absence or presence of starch in the intermediate tissue of the scutellum.

Later on, when discussing the secretory power of the scutellum, we shall have occasion to refer to another method for determining if a particular substance has any nutritive value.

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* Owing to the large excess of moisture present, growth was very rapid in this case, and the increase in weight correspondingly great. Under the ordinary conditions of the malting process, or of natural germination in moist earth, the dry weight of the embryos would not have exceeded that of the embryos cultivated on cane-sugar.

It is evident that the phenomena we have been describing are paralleled to a certain extent by those observed by Böhm, A. Meyer, and E. Laurent in connection with the reappearance of starch in the tissues of etiolated plants when these are immersed in solutions of certain carbohydrates.

Böhm (*Botan. Zeit.*, 1883, 33, 49) in his experiments employed the leaves of *Phaseolus multiflorus* which had been totally deprived of starch by cultivation in the dark. When these were floated upon 20 per cent. solutions of dextrose and saccharose, it was found that starch reappeared and was abundantly deposited in the leaf-parenchyma.

In 1886, A. Meyer (*Botan. Zeit.*, 1886) and E. Laurent (*Botan. Zeit.*, 1886, 151) published, almost simultaneously, the results of their work in this direction, Laurent subsequently giving a more detailed account of his observations in a separate memoir published in Brussels, in 1888, entitled "*Recherches experimentales sur la Formation d'Amidon dans les Plantes.*"

Meyer, following in the main the method of Böhm, endeavoured to ascertain if the leaf, after being deprived of starch, has the power of reproducing this substance from solutions of levulose and galactose, as well as from dextrose. He found that all three of these carbohydrates are transformed into starch by the parenchymatous tissue, but that the leaves of all plants do not reproduce starch equally well from the same carbohydrate. As a general rule, the best starch-forming sugar for any particular plant is the one which occurs naturally in its tissues.

Milk-sugar and *raffinose* were found to be incapable of reproducing starch, and whilst maltose gave rise to but little starch in the leaves of the beet and of the lilac, it produced considerable quantities in the leaves of the dahlia. Mannitol, which occurs naturally in some of he Oleaceæ, gave rise to starch in the leaves of plants belonging to this natural order, whilst, in one case, dulcitol also produced the same effect. Glycerol was found to be a ready starch-former in most leaves.

Laurent (*loc. cit.*) employed the etiolated shoots of the potato, which, by immersion in water in the dark for a considerable period, had been thoroughly deprived of starch. The shoots were then immersed in the solutions, and were examined from time to time to ascertain if starch was forming in the tissue.

The general results of Laurent's experiments were very similar to those of Meyer. Out of a very large number of substances examined, only *seven* were found to be starch-forming under these particular conditions; these were *glycerol*, *dextrose*, *levulose*, *galactose*, *saccharose*, *lactose*, and *maltose*.

(9.) *Growth of Excised Embryos on Starch, and Proof that an Amylo-hydrolyst (Diastase) is Secreted by the Young Embryo.*

If freshly excised barley embryos are placed with their scutella in contact with moist barley-starch, which has been spread in a thin layer upon a porous tile partially immersed in water, transitory starch can be detected within a very short time in the parenchyma of the scutellum, a certain indication that the embryo is absorbing nutritive material.

If the starch-granules in immediate contact with the exterior of the scutellum are now examined, they are found to be much acted upon, showing evident signs of erosion and disintegration.

If the layer of starch is too thick and too much water is present, this action on the starch-granules is somewhat difficult to trace in its very early stages, owing to a too rapid diffusion of the diastase given off by the embryo. A better result is obtained by confining the starch to a small portion of the plate, not much exceeding the area of the scutellum, but a still better plan is to partially embed the embryo in a 5 per cent. gelatin solution containing finely-divided barley-starch in suspension. This mixture, which we shall hereafter allude to as "starch-gelatin," is prepared by adding finely-divided barley-starch to a slightly warmed solution of the gelatin, and stirring until the mixture is on the point of solidifying. The embryos are placed upon the surface of the "starch-gelatin" when this is on the point of setting, using a gentle pressure in order to bring every part of the convex surface of the scutellum in contact with the cultivation medium. In this manner it is possible, by the examination of small pieces of the starch-gelatin cut out from beneath the growing embryo, to follow the gradual progression of the solvent action upon the starch-granules.

This action is seen to arise, first of all, at the limiting surfaces of the scutellum and starch-gelatin, and to be independent of the presence of micro-organisms. It is true that such a mixture of starch and gelatin, when left to itself for a sufficient time, has its starch-granules ultimately affected by the micro-organisms which arise in it, but the intensity of this action is much less, and the time required to produce it is much greater, than in the case of disintegration effected by the growing embryo.

The action of the barley embryo is not confined to its own particular starch. We have made cultivations, in the manner described, upon gelatin mixed with starches from the following plants:—*barley*, *wheat*, *rice*, *maize*, *potato*, and *bean* (*Phaseolus multiflorus*), and have found that, whilst the disintegration of the barley-starch proceeds the mo rapidly, the starches of *wheat*, *rice*, and *maize* are also readily attacked. In the case of *maize*, this action is manifested by the appearance of numerous radial striæ, which give the polygonal granule a pseudo-crystalline appearance. Much the same effect is also observed in the case of *rice-starch*, the transparent polygonal grains rapidly becoming dark and almost opaque from the same cause. The starches of *potato* and *bean* altogether resist the action of the barley embryo.

The action of the embryo upon ungelatinised starch is distinctly correlated with its growth; or, perhaps, it is more accurate to say that its amylo-hydrolytic power is intimately connected with the metabolic activity of the cells composing it. If excised embryos are exposed for a short time to the influence of chloroform vapour, and are then placed upon starch-gelatin, it is found that they are now incapable of growth, and it is impossible to detect any action upon the underlying starch-granules, although the conditions are still favourable for the outward diffusion into the starch-gelatin of any soluble portions of the cell-contents.

The microscopical evidence afforded by these experiments distinctly points to the liberation of a starch-dissolving enzyme by the growing embryo; but before considering the point of origin of this enzyme it will be well to adduce independent *chemical* evidence in support of this. This can only be satisfactorily obtained by an actual quantitative estimation of the diastase produced, and it is necessary at the outset briefly to describe the methods which render such an estimation possible.

In the year 1879 it was pointed out by one of us and Heron (Trans., 1879, 654) that the relative starch-transforming powers of two infusions of malt can be ascertained by plotting a time-curve of each reaction, and measuring the amount of degradation of the starch occurring in each case in a given time.

The subject was independently investigated by Kjeldahl (*Résumé du Compte rendu des travaux du Laboratoire de Carlsberg*, 1, 129, 1879), who showed that, in order to make an accurate comparison of diastatic activity under these circumstances, it is necessary to control the reaction within certain limits. He established what he terms his "law of proportionality," which may be briefly expressed as follows:—When equal volumes of two diastatic solutions, which are to be compared, are allowed to act upon solutions of *soluble-starch*, under identical conditions of time, temperature, and concentration, then the cupric-reducing power of the two solutions, taken at any given moment, is a measure of the relative starch-transforming powers of the diastatic solutions, *providing the cupric-reducing power is not allowed to exceed* κ 25—30.

The starch solution employed by Kjeldahl was prepared by acting upon a starch-paste with a small quantity of malt-extract, and arresting the action by boiling as soon as limpidity was produced. The resulting liquid was used in the manner above indicated, a correction being applied for the small amount of reducing substances present.

C. J. Lintner (*J. pr. Chem.*, **34**, 378) has suggested certain modifications of this method, which consist in employing a solution of soluble-starch, prepared with dilute hydrochloric acid instead of with malt-extract, and in using a volumetric method for determining the reducing power, which is essentially the same as that proposed by Reischauer.

Lintner's method, although extremely useful for certain purposes, does not admit of sufficient accuracy for the determinations which we are now considering, and we have consequently in all cases employed a gravimetrical method for estimating the reducing power. The following is a brief sketch of the application of the method :—

Let it be supposed that we require to determine the relative amylo-hydrolytic activity of two series of embryos, or parts of embryos, before and after germination. The parts required for comparison are first carefully dissected out (the actual number taken being dependent on the expected diastatic activity), and are then rubbed down with a little chloroform-water,* and made up to a uniform volume of 25 c.c. In experimenting with some portions of the seed it is necessary to dry them at a low temperature, and then to reduce them by grinding. The mixture is allowed to stand for 24 hours, with occasional shaking, and is then filtered. A certain definite quantity of the clear filtrate is then added to 25 c.c. of a solution of soluble-starch of about 2·5 per cent. concentration, made by Lintner's acid method. The amount of amylo-hydrolytic solution added must be so regulated as to confine the reducing power of the transformed solution within the limits of the "law of proportionality;" this often necessitates a preliminary experiment, the approximation to the quantity required being rapidly obtained by Lintner's volumetric method.

The action is allowed to proceed at 30° C. for *exactly an hour*, when further transformation is arrested by boiling. The cupric-reducing power of the solutions is then determined gravimetrically, and after correcting for the initial reducing power of the starch solution, and where necessary also for any sugars which have been introduced with the diastatic solution, the total amount of reducing power exerted by the whole volume of each of the diastatic solutions is calculated.

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* This is a solution of chloroform containing 5 c.c. in 1 litre of water. We have found that chloroform does not influence the action of the soluble enzymes of germinated barley, whilst, on the other hand, it inhibits the growth of micro-organisms.

The numbers thus obtained are proportional to the relative amylo-hydrolytic activities of the solutions.

For the sake of uniformity, and for purposes of ready comparison, we have always throughout this paper expressed the diastatic power in terms of grams of CuO per 50 individual corns, embryos, or parts of embryos, &c.

The diastatic power of any medium upon which the embryos may have been cultivated is determined substantially in the same manner, the results in this case being also expressed in terms of 50 embryos.

We may now consider the application of this method to the determination of the diastase which is liberated from excised embryos when they are grown in water-culture or upon gelatin, and see how far the conclusions based upon micro-chemical examination are confirmed by independent chemical methods.

The embryos of 50 corns of barley which had been soaked in water for 24 hours were macerated as described above, and the clear liquid was found to have a total diastatic power equivalent to 0·005 gram CuO, due correction having been made for the reducing sugars present, which in this case amounted to the equivalent of 0·0304 gram CuO.

As the number expressing the diastatic power falls within the limits of error of the method, we may consider that the embryos of the resting seed contain no amylo-hydrolytic enzyme, or at most only a trace.

Two sets of 50 embryos, excised from the same barley, were then germinated in water-culture under the following conditions:—

Series A upon moistened glass-wool.

Series B upon 5 per cent. gelatin solution.

At the end of four days the diastatic activities of the embryos and of the culture media were determined, with the following results:—

	Grams CuO.	Total CuO.
Series A—		
Diastase in *embryos* equivalent to......	0·0874	0·1484.
„ the *water* equivalent to	0·0610	
Series B—		
Diastase in *embryos* equivalent to......	0·0732	0·1634
„ the *gelatin* equivalent to....	0·0902	

It is clear from this experiment, which is only one of many of a similar nature, that the chemical methods are entirely confirmatory of the micro-chemical, and afford unmistakable evidence of the production of an amylo-hydrolytic enzyme during the germination of the embryo, and of a diffusion of this enzyme into the culture-medium.

The appearance of the soluble ferment outside the embryo cannot be regarded as the result of a mere straining out of an enzyme pre-existent in the tissue, for we have seen that the ungerminated embryo contains but a mere trace of soluble amylo-hydrolytic ferment; the enzyme must consequently have been derived from some material stored in the embryo during its resting stage, and which has been modified in its passage outwards; in other words, the production of the amylo-hydrolytic enzyme is a *secretory* and not an *excretory* process.

(10.) *The Secretion of Diastase is localised in the Absorptive Epithelium.*

We have now to consider if the secretion of an amylo-hydrolytic enzyme can be traced to any specialised tissue of the embryo, or if it is due to the combined metabolic processes of the whole of the cells.

The curious analogy which the columnar cells of the so-called "absorptive epithelium" of the scutellum bear to certain secretory epithelial cells of the alimentary tract of animals led us, at an early stage of our enquiry, to suspect that their functions were something more than merely absorptive, and this idea was much strengthened when we found that the histological changes in the columnar cells during germination are closely paralleled by those which occur in animal epithelium whilst actively secreting, and in the glandular cells of *Dionæa muscipula* under like circumstances, as determined by Gardiner (*Proc. Roy. Soc.*, 1883, 1).*

The direct experiments which are recorded below were made with a view to test how far the columnar or "absorptive" epithelium can really be regarded as a secretory tissue. The results leave no doubt that one of the specialised functions of these cells is the elaboration of an active form of diastase, the absorptive function being of comparatively secondary importance.

When a freshly excised embryo is taken from a grain of barley which has been previously softened in water, and is partially embedded, scutellum upwards, in any of the usual embedding materials of low melting point, it is possible, by very gently scraping with a finely pointed scalpel, completely to remove the absorptive epithelium from the surface of the scutellum. After considerable practice this operation, which should be conducted with the aid of a lens, or under a dissecting microscope, may be carried out without any serious injury to the underlying parenchyma of the scutellum.

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* At some future time we shall have occasion to dwell more at length on the histological changes occurring in the epithelial cells during germination, and their points of resemblance to the changes observed in certain secretory glandular cells of animals.

If an embryo, thus deprived of its epithelium, is placed upon a culture medium containing any readily assimilable carbohydrate, such as cane-sugar or dextrose, the young plant grows as readily as it would have done in its unmutilated state, the ground tissue of the scutellum absorbing and making use of the nutrient just as freely as if the epithelium were still attached.

When, however, such a mutilated embryo is placed upon a "starch-gelatin" mixture, it is found to have *entirely lost its former power of eroding and dissolving the starch-granules.*

The same remarkable difference in the action of unmutilated embryos, and of those deprived of their epithelium, is also observed when these are grown side by side upon a stiff starch-paste. In the course of a few hours the embryos which retain their epithelium are found to have liquefied the starch-paste around them, and to have embedded themselves to a depth of several millimetres, whilst the germs deprived of their epithelium *have failed to produce any liquefaction.*

The epithelium retains to a limited extent its power of secreting an amylo-hydrolytic enzyme even after its removal from the embryo. This can be demonstrated by cutting thin sections tangential to the surface of the scutellum, and placing them on "starch-gelatin." Distinct action on the underlying granules takes place in those cases in which the section includes any portion of the epithelium, but no corrosion of the starch takes place if the epithelial cells are absent.

(11.) *The Secretion of Diastase by the Columnar Epithelium is increased by the Presence of a Small Quantity of Acid.*

This was shown by a comparative determination of the diastase liberated during the cultivation of excised embryos upon (1) neutral gelatin medium, and (2) the same medium rendered very slightly acid by formic acid:—

A. 50 barley embryos cultivated on *neutral* 5 per cent. gelatin medium for three days.

Diastase in embryos equivalent to	0·0708	gram CuO.
„ medium „	0·0478	„
Total diastase secreted equiv. to ..	0·1186	„

B. 50 barley embryos cultivated for three days upon gelatin medium to which had been added 0·0065 per cent. formic acid.

Diastase in embryos equivalent to	0·0904	gram CuO.
„ medium „	0·0546	„
Total diastase secreted equiv. to ..	0·1450	„

(12.) *The Secretion of Diastase by the Columnar Epithelium not Stimulated by the Presence of Starch.*

As we have very good reason to believe that the secretory power of certain animal glands is stimulated by the mere presence of the digestible material, it seemed by no means improbable that the flow of amylo-hydrolytic enzyme from the glandular cells of the scutellar epithelium might be influenced by the presence of *starch*, either in the granular form or as *soluble-starch.* We have made numerous experiments with the object of determining this point, and have quantitatively estimated the diastase liberated in the presence and absence of these substances, but our results have in all cases indicated that *starch does not stimulate the epithelial cells to increased secretion.* The following are the results of two series of such experiments :—

	Total diastase formed expressed as grams CuO.
Expt. I.—	
A. 50 barley embryos germinated upon 5 per cent. solution of gelatin for four days	0·1634.
B. 50 similar embryos germinated for the same period on "*starch-gelatin*"................	0·1596.
Expt. II.—	
A. 50 barley embryos germinated upon 5 per cent. gelatin solution for six days	0·2432.
B. 50 similar embryos germinated for the same period on "*starch-gelatin*"................	0·2209.

(13.) *The Secretion of Diastase by the Columnar Epithelium is Inhibited by the Presence of a Readily Assimilable Carbohydrate.*

We have seen how readily the granules of barley-starch, after suspension in gelatin, are attacked and dissolved under the influence of germinating barley embryos. If, however, there has been previously added to the gelatin medium a small quantity of cane-sugar, the starch is protected in a remarkable manner, and no sign of disintegration of the granules can be detected as long as any sugar remains unabsorbed by the growing plantlet.

We have convinced ourselves by direct chemical examination, both of the embryos so cultivated and of their culture medium, that this phenomenon is due to an inhibitory action of the carbohydrate; it is not that the secreted diastase is rendered inactive by the sugar present, but that *under these particular conditions the epithelial cells of the scutellum do not secrete any amylo-hydrolytic enzyme.* We have found this inhibitory action confined to those carbohydrates which our previous experiments have shown to be directly assimilable by the embryo, whilst solutions of substances which are not directly assimilable, such as *mannitol* and *milk-sugar*, have no such inhibitory effect, diastase being freely secreted in their presence, and the starch-granules dissolved in the usual manner.

So strongly marked are the differences between the assimilable and non-assimilable carbohydrates in this respect that this method may be employed for determining if the particular substance has any value as a food material for the young plant.

This curious inhibitory action of assimilable substances is quite independent of any influence exercised by the main axial organs of the embryo, for it is equally evident when tangential sections of the scutellum are employed, providing these include any portion of the epithelium, and the action can also be demonstrated in the case of an embryo still attached to its natural endosperm, as the following experiments prove.

Some grains of barley, after being steeped in water for 24 hours, had their apical (distal) ends cut across, and were then planted, with the embryo (proximal) ends uppermost, in loosely-packed glass-wool saturated with—

(1.) Distilled water.
(2.) A 3·5 per cent. solution of cane-sugar.

By this arrangement the water and sugar solution are able readily to diffuse through the parenchyma of the endosperm and to reach the growing embryo.

Vigorous and normal growth of the embryos took place in each case, but at the end of four days, on making sagittal sections of the grain, very great differences could be detected in the appearance of the two sets of endosperms. In (1), where water only had been employed, the endosperm was completely disintegrated owing to the dissolution of the walls of the starch-containing cells, whilst action on the starch-granules could be detected for some distance from the scutellum. In (2), on the other hand, where cane-sugar was present, the greater part of the tissue of the endosperm was still as tough and resistant as before germination, whilst disintegration of the starch-granules was traceable only to an extremely small distance inwards. After 24 hours' further growth the differences between the two series were still more marked, proving beyond all doubt the inhibitory action of the cane-sugar, even when the embryo is still attached to its natural host. This influence of the sugar is not confined merely to the secretion of the amylo-hydrolytic enzyme, but affects also the dissolution of the cell-walls, which is almost completely arrested in the presence of the carbohydrate.

The diminution, and even total suppression, of the amylo-hydrolytic secretionary functions of the epithelium by assimilable carbohydrates is a fact of the highest physiological significance. It is evident that the power of secretion is, in some way or other, so adapted to the requirements of the young plant, as to be only exercised when the supply of soluble tissue-forming carbon-compounds begins to fail. As the supply of these substances becomes less, the solid reserve materials are acted upon by the secreted enzyme, the production of which is doubtless further controlled by the products of its own reaction, a wasteful expenditure of the secretion being thus prevented.

The secretion of active diastase by the epithelium may be regarded to some extent as a *starvation phenomenon.*[*]

(14.) *On the Existence of a Cellulose-dissolving Enzyme* (*Cyto-hydrolyst*) *in the Germinating Seed of the Grasses.*

We have already seen that in the early stages of germination of barley the parenchymatous cell-walls of the endosperm are disintegrated and ultimately dissolved, and that the disappearance of the cell-wall always precedes any visible attack upon the contained starch-granules.

It has been long known that the cellulose which is stored up in seeds is capable of being made use of by the growing plant, but the precise method by which this is brought about has yet to be shown.

The seed of the date (*Phœnix dactylifera*), in which the highly-thickened cell-walls of the endosperm form by far the greater part of the reserve material, has been subjected to careful examination by Sachs (*Bot. Zeit.*, 1862), who has shown that the absorption of the

[*] The phenomena here recorded are closely paralleled by those observed by Wortmann (*Zeit. physiol. Chem.*, 6, 287), who found that a certain bacterium has the power of excreting a starch-dissolving enzyme when starch-granules are the only available food, but that no secretion of enzyme takes place if sugar or tartaric acid is offered to the organism along with the starch. De Bary ("Lectures on Bacteria," p. 71) states that "similar facts are recorded of *Bacillus amylobacter*, which according to Van Tieghem, when fed with glucose, leaves the cellulose which is presented to it at the same time untouched, but decomposes it and takes it in as food if no source of more readily assimilable carbon is available."

reserve-cellulose during germination is brought about by an extension of the cotyledon, which very gradually encroaches upon the endosperm. The surface of this advancing portion of the cotyledon is covered with a well-marked epithelium, which, according to Sachs, probably emits some special substance which provokes the absorption of the cellulose, but he does not appear to have made any direct experiments in support of this view. We find that this epithelium consists of two rows of cuticularised cells with finely granular contents. The cells of the outer layer are columnar in form (palisade cells), and are arranged perpendicular to the surface of the cotyledon. In general appearance, both in transverse and longitudinal sections, these cells, especially those of the outer layer, resemble in many respects the columnar epithelial cells of the scutellum of the Grasses; in the latter case, however, the epithelium is fixed in position, whilst in the case of the date the epithelial cells increase in number, and are gradually pushed forward as the reserve-cellulose of the endosperm is absorbed.

During germination of the date, there is abundant microscopical evidence of dissolution of the cellulose in the immediate neighbourhood of the epithelium, but the action extends only a very short distance into the endosperm.

An attempt has been made by J. R. Green (*Phil. Trans.*, **178**, 57, 1887) to extract a soluble cellulose-dissolving ferment from the germinating date. A glycerin extract of the cotyledons was found to have a slight action upon cotton fibre after two days' digestion, whereas the previously-boiled extract had no such action. Green concludes that the glycerine extract contains a trace of enzyme capable of hydrolysing cellulose to a sugar, but that the amount of ferment so procurable is very small, and that the disappearance of cellulose in germination is not due to an isolable enzyme, but to a gradual destruction of the reserve material by the epithelium, in the cells of which the ferment exists.

We have carefully repeatod this experiment upon the seeds of the date, which had been germinated for eight weeks, but instead of employing a glycerol extract, as suggested by Green, we prepared an ordinary aqueous extract of the cotyledons, in which the growth of micro-organisms was prevented by the addition of a little chloroform, for we have always found that an *aqueous* extract of a vegetable or animal tissue containing a soluble enzyme has a hydrolytic power far superior to that of an extract made with glycerol. In this solution were immersed thin sections of *potato*, *carrot*, and *turnip*, whose parenchymatous cell-walls we had previously found to be very susceptible to the action of cellulose-dissolving enzymes. Neither these sections, nor thin sections of the endosperm of the date, showed the slightest signs of being acted upon, even after very prolonged digestion.

Although we have been unable to confirm Green's statement that a soluble cellulose-ferment can be extracted from the growing cotyledon, we are not prepared to deny the existence of such an enzyme. We have seen how, in the germinating date, the visible action on the cellulose can be traced only to a very small distance from the epithelium, which is supposed to be the seat of the secretion of the enzyme. This fact, coupled with the extreme slowness of the disappearance of the reserve-cellulose, even under the most favourable conditions of temperature, renders it highly probable that the ferment is used up almost as fast as it is formed, and that there is no accumulation of the enzyme, as there is in certain other seeds to which we shall presently refer. Under these circumstances the amount of enzyme existing in the seed at any one time would be very small.

Although the endeavours to isolate a soluble cellulose-ferment from the date have only been partially successful, we are now able to show for the first time the existence of a considerable amount of such an enzyme in the germinating seeds of the Grasses.

If sections of barley of varying thickness are immersed in a cold-water extract of *air-dried* barley-malt of sp. gr. 1·030 to 1·040, in the course of a few hours they undergo considerable alteration.

If the sections are thin, the parenchymatous tissue of the endosperm portions, within less than 24 hours, is completely disintegrated, the cell-walls either entirely disappearing or remaining in a much swollen and altered form as mere "ghosts."* In the thicker sections, disintegration can be traced to a depth 1·5 to 2 mm., and this breaking down of the tissue proceeds rapidly if the digestion with the malt-extract is continued. The addition of a little chloroform or thymol admits of the experiments being carried on for any length of time that may be required, without the disturbing influence of micro-organisms.

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* The following method is well adapted for observing under the microscope the gradual dissolution of the cell-wall of the endosperm of the Grasses. Thin sections are made, which are cleared of their starch by treatment with saliva in the way already mentioned (p. 462). These sections, in which the cell-walls are rendered very apparent, are then put on a thin cover-glass with a drop of a cellulose-dissolving liquid (either cold-water malt-extract made with air-dried malt, or a solution of the precipitated cellulose-dissolving enzyme), and examined by the ordinary "hanging-drop" method, the slide being maintained at a temperature of about 25—30° C. It is advisable in all cases to add a little thymol to the liquid. In this way it is easy to follow all the stages of dissolution of the cell-wall, a portion of which can, if required, be kept under continuous observation. We shall, in a future part of our paper, have occasion to refer in detail to the results obtained on the seeds of various Grasses examined by this method.

The alteration of tissue in these experiments is exactly similar, both macroscopically and microscopically, to those which take place in the endosperm during the early stages of germination. This is shown in a very striking manner by immersing in the malt-extract grains of barley which have been deprived of their embryos. Disintegration commences in the "depleted cells" of the endosperm adjacent to the scutellum, and progresses rapidly in a distal direction, the cells of the endosperm losing their coherence and becoming "mealy," just as in natural germination; we have in fact a partial "malting" without the aid of germination.

That these changes are due to *the presence of a soluble ferment* or enzyme in the malt-extract is proved by the fact that previous heating of the extract totally and permanently destroys its activity as a cellulose-dissolving agent; and, further, it is equally certain that the enzyme is not pre-existent in the resting seed, but is a product of germination, since an extract of ungerminated barley has no action on cellulose.

The cellulose-dissolving enzyme can be precipitated from a cold-water extract of an air-dried malt by means of alcohol, the method being similar to that adopted for the preparation of diastase. On dehydration with absolute alcohol, and drying in a vacuum, the resulting white powder, which is soluble in water, is found to be actively *cyto-hydrolytic** as well as *amylo-hydrolytic*.

The cyto-hydrolytic power of the crude enzyme so prepared is considerable, especially if the solution is made very feebly acid with formic or acetic acid. Sections of barley or of wheat placed in such solutions rapidly exhibit all the phases of disintegration which are observed when malt-extract is used. The cuticularised peripheral aleurone-cells resist the action of the enzyme for a considerable time, as in the case of natural germination, but the cell-walls of the starch-containing parenchyma rapidly disappear, and there is also considerable action upon the "sheaf-like" cells which we have described as being the remnant of the nucellus. The comparative resistance to dissolution of the starch-containing cells of the *ventral* side of the grain is clearly shown when transverse sections are employed, the differential action being exactly similar to that already referred to as occurring in natural germination, and is probably due to a slight change towards lignification in the older cell-walls on the ventral side. The tissues of the integument, and, in fact, all those which exhibit the least signs of lignification, remain intact.

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* The word *cyto-hydrolytic* (*cf. cytoplasm* and *cytoblast*) was suggested to us by Mr. W. T. Thiselton Dyer, and has been used throughout this paper to express the hydrolytic activity of the special cellulose-dissolving enzyme. Its analogy to *amylo-hydrolytic* is sufficiently obvious. Although strictly speaking the word implies the disintegration of the whole cell (κύτος) and its contents, we have etymological grounds for limiting its application to an action upon the cell-*wall*, for exactly the same limitation of meaning has taken place in the derivation of *cutis* from κύτος. The word which originally suggested itself to us was *xylo-hydrolytic*, but this implies that the enzyme has an action upon lignified cellulose, which is certainly not the case.

The cyto-hydrolytic enzyme of germinated barley has a decided solvent action upon the endosperm-cellulose of all the Grasses we have examined, even upon the abnormally thickened cell-walls of *Bromus mollis*, but, in such cases as this, solution takes place more slowly than when the walls of the parenchyma are of ordinary thickness.

We have examined the behaviour of the enzyme towards the seeds of other natural orders of plants containing reserve-cellulose in the form of highly thickened cell-walls, but have never been able to determine any trace of solvent action even after prolonged digestion. This is the case with *Phœnix dactylifera*, *Asparagus officinalis*, *Coffea arabica*, and *Allium cepa*, all of which contain cellulose giving the yellow coloration with iodine; and it is equally true of the seeds of the following plants which possess thickened cell-walls of *amyloïd* cellulose affording a dark-blue coloration with iodine: *Impatiens Balsamea*, *Tropæolum majus*, and *Primula Webbii*.

Although the action of the cyto-hydrolytic enzyme of germinated barley appears to be confined to its own natural order as regards the cellulose of *seeds*, such is not the case with regard to parenchymatous cellulose from other parts of the plant.

When sections of *potato* are immersed in a dilute solution of the enzyme, to which a little chloroform or thymol has been added, they lose their coherence in a few hours, and fall to pieces with great readiness. This "rotten" state is produced by a change in the cell-walls, which swell up to many times their original thickness, and become differentiated into numerous very thin lamellæ. These, after a time, partially break up and become resolved into minute spindle-shaped fragments similar to those observed during the disappearance of the cell-walls of germinating barley. In the case of the potato sections, the dissolution never appears to be quite complete, owing to the resistant action of a thin layer of the cell-wall (? the middle lamella).

We have also experimented with the parenchyma of *Jerusalem artichoke*, *carrot*, *turnip*, *apple*, and *beet*. In the case of the beet, the cell-wall is but very slightly acted upon, and in the apple not at all, whereas the parenchymatous walls of the Jerusalem artichoke, carrot, and turnip exhibit the same phenomena of stratification and dissolution as do those of the potato.

Up to the present time, we have not succeeded in preparing the cyto-hydrolytic enzyme free from diastase, but the evidence is strongly in favour of the two enzymes being perfectly distinct. This is rendered probable in the first instance by the microscopical examination of the germinating seed, in which the action upon the cellulose is seen to precede in point of time the dissolution of the starch, but it is proved beyond all doubt by the differential action of heat upon the mixed enzymes after isolation, or whilst still existent in malt-extract.

When the mixed enzymes are gradually heated with water, the cyto-hydrolytic power is rendered decidedly less energetic at a temperature of 50° C., whilst heating for half an hour at 60° almost completely paralyses its action. The amylo-hydrolytic diastase, on the other hand, even after being heated to 70° C., still possesses as much power to erode and dissolve ungelatinised barley-starch as before the application of heat, and, as was shown by one of us and Heron in a previous paper (Trans., 1879, **35**, 596), the diastatic activity of malt-extract upon starch-paste is only slightly modified at 60° C., a temperature which is almost fatal to the cyto-hydrolytic enzyme.

We are at present engaged in studying the products of the transformation of cellulose under the action of this special enzyme.

(15.) *The Cyto-hydrolyst, like Diastase, is a Product of the Growing Embryo, and is also secreted by the Columnar ("Absorptive") Epithelium.*

When excised embryos of barley are laid, scutellum downwards, upon thin sections of barley, or of potato, which have been placed upon a moistened surface, visible action upon the parenchymatous cellulose takes place within 24 hours, and is often evidenced by a complete perforation of the sections.*

In sections of barley, the phenomena of dissolution are exactly similar to those observed in natural germination, and also to those which occur when the tissue has been immersed for a short time in a solution of the isolated enzyme. These changes are independent of any residual life in the cells of the tissue upon which the embryos are placed, for they occur just as readily if the sections have been previously immersed in alcohol; and, as we have had occasion to remark in an earlier part of this paper, solution of the cell-walls takes place in endosperms which have been long immersed in alcohol, after living embryos have been "grafted" upon them.

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* In the case of the parenchyma of the potato, we have found considerable variation in the resistance to the secreted cyto-hydrolytic enzyme; these differences depend to a great extent upon the particular variety of potato employed, and also, to some extent, upon its age.

On the other hand, if the embryos, prior to being placed on the sections, have been deprived of their "absorptive epithelium" in the manner already described, *they are found to have lost all power of exercising any solvent action upon the cellulose.*[*] We are consequently justified in considering the cyto-hydrolytic enzyme as being a product of the growing embryo, and in localising its secretion, as in the case of the amylo-hydrolytic enzyme, in the columnar or so-called absorptive epithelium.

Although, as we have already stated, the cyto-hydrolytic enzyme does not dissolve cellulose which is in the slightest degree lignified, it is not entirely without action upon the cellulose of *cotton-fibre.* This is best shown by cultivating excised barley embryos upon moistened *filter-paper.*

In the course of about two days, the fibres of the paper in immediate contact with the scutellum show unmistakable signs of solvent action. They become much more swollen and transparent than those at some little distance from the embryo, the striation of the fibres is less apparent, and there is a general tendency towards a loosening of their finer elements, with here and there a distinct approach to incipient solution, especially at their ends. Independent evidence of this attack upon the cotton-fibres is afforded by the fact that the embryos develop to a greater extent when cultivated on moistened filter-paper than when grown merely upon the moistened surface of a perfectly indifferent material, such as porous earthenware or glass-wool. There can be no doubt that the filter-paper is capable, under the action of the secreted enzyme, of yielding a small amount of nutriment to the growing plantlet.

This action upon filter-paper entirely ceases when the embryo is deprived of its epithelium, and it is also completely inhibited by the presence of a small amount of cane-sugar. This influence of cane-sugar in inhibiting the secretion of the cyto-hydrolytic enzyme is also evidenced in the case of an embryo still attached to its natural endosperm, and has been already referred to when considering a similar influence upon the secretion of the amylo-hydrolytic enzyme.

Between the secretion of the cyto-hydrolytic and amylo-hydrolytic enzymes there is the closest possible analogy. Both ferments are secreted by the same epithelium, and the secretory action is in both cases strongly influenced by the presence of an assimilable carbohydrate. It is probable that the secretion of cyto-hydrolytic enzymes may be a somewhat common occurrence in plant life. Marshall Ward, in a recent paper on a lily disease produced by a species of *Botrytis* (*Annals of Botany*, **2**, 319, 1888), has recorded some highly interesting and important observations upon the secretion by the hyphæ of the fungus of a ferment which is capable of softening and partially dissolving cellulose. Certain organs of attachment, and the tips of the hyphæ, are capable at times of secreting a relatively large amount of the ferment, and in culture media this may be made to "accumulate to such an extent that the hyphæ can no longer contain it, and it causes a dissolution of cellulose at the tip of the hyphæ, and consequent extrusion of the protoplasm and enzyme in the form of drops." It is owing to the secretion of this enzyme that the tip of the hypha is enabled to penetrate the tissue of the lily, which it does by dissolving its way into the cell-wall, at the same time "swelling up the cellulose, and feeding upon the products of solution, and causing destruction of the tissues by isolating the cells as if they had been boiled."

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[*] The appearance in these experiments of Schizomycetes, especially of *Bacillus amylobacter*, is attended with disintegration of the cell-walls, but the changes referred to in the text are antecedent to the appearance of bacterial life.

From pure cultures of the fungus, Marshall Ward was able to obtain solutions which produced the same kind of swelling and dissolution of the cellulose. That this is due to a special enzyme was proved by the fact that boiling the aqueous extracts rendered them inactive; moreover, the enzyme was shown to be precipitable from such extracts by alcohol.

Bearing in mind the parasitic existence of the embryo of the Grasses during germination, the analogy between it and a fungus like the *Botrytis* is closer than might at first be suspected. It is true that the secreting tissue of the embryo cannot, like that of the *Botrytis*, penetrate its host, but in both cases the accumulation and secretion of a cellulose-dissolving enzyme is a necessary prelude to the acquisition of food material.

There is also another important point of resemblance between the embryo and fungus hyphæ which must not be lost sight of. Marshall Ward considers that his observations justify him in concluding that the enzyme is not accumulated in undue quantities at any particular place within the fungus as long as active growth and increase of surface of the fungus are going on. In other words, accumulation and secretion of the enzyme increase as the food materials of the plant decrease in amount. This is exactly what we have found with regard to secretion by the epithelial cells of the embryo—an increase of food materials diminishes or actually inhibits secretion, whilst partial starvation causes a greater flow of the enzyme.*

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* It is mentioned in the paper above referred to, that De Bary found indications of the secretion of a cellulose-dissolving enzyme by a saprophytic or parasitic fungus *Sclerotinia* (*Peziza*) *Sclerotiorum*. The expressed juices of carrots which

(16.) *The Two Varieties of Diastase, their Genesis and Distribution in the Resting and Germinating Seed.*

It was for a long time believed that the saccharifying soluble ferment which exists in sprouted grain is entirely a product of germination, and that ungerminated grain contains no active starch-transforming body. It is true that Kirchof, as far back as the year 1814 (*Schweigg. Journ.*, **4**, 108), had shown that the albumin of raw grain is endowed with some saccharifying power, but this observation appears to have been almost overlooked until Kjeldahl (*Résumé du Compte rendu des travaux du Laboratoire de Carlsberg*, **1**, 1879, 129) elaborated his method for the quantitative determination of diastase. Kjeldahl, in the course of his experiments, demonstrated the existence of an active amylo-hydrolytic enzyme in ungerminated barley, but although this has a considerable saccharifying power upon solutions of soluble-starch, it has scarcely any influence in liquefying starch-paste, a fact which, in some measure, accounts for the diastatic power of ungerminated grain having been so long overlooked, previous experiments having for the most part been made with *starch-paste.*

It is this inability to liquefy starch-paste which differentiates the enzyme of the resting seed from that of germinated grain, the latter having extremely active liquefying and saccharifying powers. We shall presently see that another great point of difference between these enzymes is found in their relative action upon ungelatinised starch.

A comparative study of the amylo-hydrolysts of raw and germinated grain has recently been made by C. J. Lintner and F. Eckhardt (*Zeitschrift f. d. gesammte Brauwesen,* 1889, 389), who caused equal quantities of extracts of barley and of malt having equal hydrolytic powers to act upon soluble-starch at varying temperatures, and expressed the results of the reactions in the form of curves, of which the abscissæ represented the temperature and the ordinates the reducing power. The products of the reaction were in both cases maltose and dextrin, but the forms of the two sets of curves differed very materially from each other, so much so, in fact, as to indicate a radical difference in the nature of the two diastases. Whilst the optimum temperature for a conversion with malt-diastase lies between 50° and 55°, that of barley-diastase is between 45° and 50°; and, moreover, the hydrolytic power of barley-diastase at 4° is as high as that of malt-diastase at 14·5°.

We have endeavoured to obtain some information about the origin

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had been rotted under the influence of the fungus had a marked action upon the cell-walls of carrot, bean, or seedlings of *Brassica.*

and distribution of the diastase of ungerminated grain, and with this object in view have made a large number of comparative experiments upon unripe barley taken at different stages of development.

At the outset, it appeared most probable that this diastase owed its origin to the epithelium of the scutellum acquiring secretory powers at a very early stage of its development, and that the solution and disappearance of endosperm starch lying in front of the advancing scutellum might be owing to this fact. It is manifest, however, that if such is the case the functions of the young epithelium in the developing seed must be very different from those which it manifests in the ripe and germinating grain, since, as we have already shown, the starch-granules, in the former case, are not disintegrated but symmetrically dissolved, whilst the cell-walls of the parenchyma are not dissolved but merely compressed closely together.

When barley in different stages of development is taken fresh out of the fields, we have invariably found, on testing in the usual way by the starch-gelatin method, that the epithelium of the excised and immature embryos is incapable of secreting any enzyme which will act upon the starch-granules. This is the case even when embryos have been selected from corns which are in every way morphologically mature, *providing, however, that ripening has not advanced to the point of partial desiccation.* We have found that the expulsion of moisture has a very remarkable influence upon the secretory functions of the embryo, both as regards the amylo-hydrolytic and cyto-hydrolytic enzymes. Comparative experiments have clearly shown us that the potentiality of secretion is of late development in the growing embryo, and that actual secretion cannot be induced in the epithelium even then without previous expulsion of moisture.* It is quite clear from these facts that the presence of a diastase in raw grain cannot be due to an epithelial secretion of the same kind as that observed in germination; nevertheless, that the occurrence of the soluble ferment is in some way intimately connected with the development of the embryo is shown by the fact that it increases in quantity in the grain *pari passu* with the increase in size of the embryo, and also that its distribution within the seed is confined mainly to the proximal end of the grain, that is, to the end including the embryo.

The increase in the amount of amylo-hydrolytic enzyme in barley during development is shown by the following experiments, made upon the grain at different periods of growth:—

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* It has long been known to practical maltsters that barley from which the original moisture has not been fully expelled by natural or artificial drying germinates but very imperfectly. We have now for the first time an approach to an explanation of this fact.

(1). Endosperm about one half developed.
(2). Endosperm two-thirds developed.
(3). Endosperm fully developed, but grain not ripened.

Diastase Estimated in 50 *Corns.*

(1.)	Equivalent to	4·390 gram CuO.
(2.)	„	7·833 „
(3.)	„	9·675 „

The following experiment illustrates the *distribution* of amylo-hydrolytic enzyme in raw barley, and brings out the fact that the major part of the soluble ferment is confined to the *proximal* end of the seed :—

In 50 corns of a ripe (Californian) barley, *after steeping in water.*

	Grams CuO.
Diastase in proximal halves of endosperm	1·715
„ distal „ „	0·610
Total	2·325

An independent determination of the diastase in 50 whole corns of the same barley gave a result equivalent to 2·486 grams CuO.

We shall be in a better position to discuss the origin of the diastase of ungerminated grain after a consideration of the facts recorded in the following section.

(17.) *Distribution of Diastase in the Germinating Seed.*

The large increase of the more active amylo-hydrolytic enzyme which occurs in barley during germination is no doubt principally due to a secretion by the columnar epithelium of the growing embryo. There is a steady accumulation of starch-liquefying diastase in the endosperm, and this in the course of time permeates its whole tissue, the ready passage of the enzyme through the contents of the grain having been enormously facilitated by the previous destruction of the cell-walls by the cyto-hydrolytic enzyme.

The following experiment illustrates very clearly the distribution of diastase in the germinated grain, and a comparison with the results previously given for ungerminated grain gives a fair idea of the increase of amylo-hydrolytic enzyme brought about by germination :—

Distribution of Diastase in Barley germinated for Seven Days under the ordinary condition of the Malting Process.

	Grams CuO.
Diastase in 50 half endosperms (proximal)	9·7970
" " " (distal)	3·5310
" radicles of 50 corns	0·0681
" plumules "	0·0456
" scutella "	0·5469
Sum of diastase in separate estimations	13·9886
Diastase determined in 50 *whole* corns of the same barley	13·7260

The accumulation of diastase in the proximal ends of the endosperm, that is, in the immediate neighbourhood of the embryo, is well shown in this experiment, but the principal interest centres in the numbers which indicate the relative diastatic activity of the various organs of the *embryo*. These were carefully dissected from each other and a separate determination made for *plumules*, *radicles*, and *scutella*. We see that the *scutellum* contains by far the greater proportion of the total diastase of the embryo, but it will be noticed that both *radicles* and *plumules* also possess a small share of activity in this respect. We have found, however, that whilst the enzyme of the scutellum, like that of the endosperm, is capable of liquefying *starch-paste* with great rapidity, the enzyme of the plumules and radicles resembles that of raw grain, inasmuch as it is incapable of acting upon *starch-paste*, even when its amylo-hydrolytic power in solution, estimated by its action on *soluble-starch*, is made equal to that of an infusion of the scutella. The scutellum owes its power of liquefying starch-paste and eroding and disintegrating starch-granules* to its epithelium, and it is this tissue only which has the power of producing this highly active form of diastase.

The comparatively small quantity of the less active form of diastase existent in the plumules and radicles is doubtless connected with the disappearance of the small grains of *transitory starch*, which crowd certain portions of their tissue when the embryo is well supplied with nutriment. There seems every reason to believe that the enzyme in these cases takes its rise in the cell-protoplasm in which the starch-grains are embedded; and that it is a product of the metabolic activity of the cell in the same sense that *invertase* is a product of the yeast-cell.

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* We have always found the power to liquefy starch-paste, and to erode the starch-granule to go hand in hand. A diastase which will liquefy starch-paste will, under favourable conditions, also disintegrate the starch-granule, and *vice versâ*. It is always safe to predict that a non-liquefying diastase will not attack the granule by pitting and disintegration, and that a diastase which will not so act on the granule will not liquefy starch-paste.

It has been noticed by many observers that certain tissues of plants, such as buds and leaves, which contain transitory starch, all give indications of containing an amylo-hydrolytic enzyme. Most observations agree in defining this enzyme as having feeble diastatic powers as compared with that of germinated grain, but we must bear in mind that most of the experiments have been conducted with *starch-paste*, upon which this special variety of diastase acts with difficulty; there is no doubt that when such experiments are repeated, using solutions of soluble-starch instead of starch-paste, tissues containing transitory starch will be found to contain a much larger proportion of amylo-hydrolytic enzyme than has been previously imagined.

The enzyme produced within the cell for facilitating the translocation of starch in the tissues differs so widely from the more active form which is secreted by a specialised tissue, such as the scutellar epithelium of the Grasses, that it becomes necessary to adopt different names for the two enzymes. We shall in future speak of the less active amylo-hydrolytic enzyme as "*diastase of translocation*," or "*translocation diastase*," whilst the more active form, which is a secretion of certain specialised cells, we shall refer to as "*diastase of secretion*."

We are now in a better position to understand the origin of the diastase of the resting seed. In the case of barley, and doubtless also, of all the Grasses, this enzyme has the properties of "translocation diastase;" it can neither liquefy starch-paste nor erode the starch-granule. During the invasion of the young parenchyma of the endosperm by the developing embryo, the cells bordering on the embryo are, as we have seen, emptied of their starch, and, in fact, of all their contents. The disappearance of the starch and its symmetrical dissolution resemble what is seen during the disappearance of transitory starch, and we cannot doubt that the changes are brought about by the same means, that is, a production of "translocation diastase" in the parenchymatous cells of the endosperm. How this is initiated is not at present clear, but it is possibly brought about by a small amount of acid from the growing embryo acting upon a *zymogen* in the endosperm cells.

It is the unused residue of the enzyme so produced which constitutes the diastase of *ungerminated* grain.

(18.) *The Mother Substance of the "Diastase of Secretion" accumulated in the Germinating Seed must be principally derived from the Endosperm.*

This is sufficiently proved by the results we have obtained in the quantitative determinations of diastase secreted by excised embryos grown on cultivation media. Although the production of diastase under these conditions is considerable, when the weight of the embryo is taken into consideration, yet it falls far short of the total quantity which is found accumulated in the endosperm, when the embryo is cultivated under its natural conditions. The secretory powers of the separated embryo come to an end as soon as the limited amount of reserve material contained within it is exhausted.

We shall have occasion to show, in a future communication, that there is, under natural conditions of germination, a rapid flow of nitrogenous material from the endosperm across the columnar epithelium, and it is doubtless from a portion of this material that the glandular cells are able o elaborate the greater part of the diastase which flows steadily outwards into the endosperm, where it accumulates. It is highly probable that the production of at least a portion of the cyto-hydrolytic enzyme may be accounted for in the same way.

The experiments of Reychler (*Ber.*, **22**, 414), and of C. J. Lintner and Eckhardt (*Zeitschr. für das gesammte Brauwesen*, 1889, 389), upon so-called "artificial diastase," indicate that an amylo-hydrolytic enzyme may be formed from the gluten or mucedin of wheat by the action of dilute acid. The ferment so prepared has all the properties which we have ascribed to "*translocation diastase.*"

It seems highly probable that this form of diastase may arise in living tissue, by the action of the acid cell-sap upon some zymogen existing in the protoplasm, but the origin of the more active "*diastase of secretion*" cannot be explained in this simple way.

(19.) *Action of "Diastase of Secretion" upon Ungelatinised Starch.*

The statement made by O'Sullivan in 1876 (*J. Chem. Soc.*, 1876, ii, 133) that ungelatinised starch is not acted upon by malt-extract was confirmed three years later by one of us and Heron (Trans., 1879, 621), when the conclusion was arrived at that, as long as the outer layer of the granule is intact, "pitting" and disintegration cannot be produced by artificial means, this form of dissolution being inseparable from the action of the living cell of the germinating grain in which it occurs.

It was only after the publication of the last-mentioned paper that the attention of one of us was directed to a memoir by Baranetzky

("Die stärkeumbildenden Fermente," Leipzig, 1878) in which he gives the results of a number of experiments on the comparative rate of action of malt-diastase upon starches of various kinds.

He found that ungelatinised potato-starch, which had been exclusively used by O'Sullivan and ourselves, is highly resistant to diastase, whilst most of the starches of grain are readily acted upon, with all the phenomena which attend their natural solution in the germinating seed.

We have frequently repeated these experiments of Baranetzky, and can fully confirm their accuracy.

Well washed and purified barley-starch is, in a few days, "pitted," disintegrated, and dissolved by a cold-water extract of air-dried barley-malt, or by a solution of precipitated diastase prepared from such a malt. The action in the latter case, as has been shown by Baranetzky, is much facilitated by the addition of a very minute quantity of acid.

In the following experiment, well-purified, ungelatinised *barley-starch* was allowed to remain in contact with a solution of precipitated malt-diastase to which 0·0065 per cent. of formic acid had been added. It may be stated that an acid of this degree of dilution has no action whatsoever upon barley-starch. A trace of chloroform was added to prevent putrefactive changes, and the action was allowed to proceed at ordinary temperatures for a period of 20 days, at the end of which time the solution was analysed.

Sp. gr. of solution, 1013·32.

Optical activity in 200 mm. tube, 24·6 div.

Cupric reduction per 100 c.c. = 4·297 grams CuO. This is equivalent to 3·194 grams maltose, which would give a deflection of 24·9 divisions, against 24·6 actually observed. We may conclude, therefore, that the whole of the optically active substance is *maltose*, which, in this case, amounts to 92·4 per cent. of the total solids which have gone into solution.

(20.) *A Consideration of the Origin of the Hydrolytic Enzymes of Germinated Grain.*

We have seen how the isolated embryo may, under artificial conditions, be made to bring about identically the same changes in parenchymatous cell-walls, and starch-granules, as are observed in the endosperm during natural germination; we cannot but conclude, therefore, that these phenomena, which are amongst the most important of the visible changes produced under natural conditions, owe their origin to the growing embryo, and more particularly to the extraordinary secretory functions of the scutellar epithelium. There are, however, two other views which have been advanced within the last few years to account for the observed changes in the endosperm of growing seeds, and to these we must now briefly refer.

In 1886, Frankhauser (*Der Bund. Berne*, **37**, No. 26) in recording the results of an inquiry into the nature of diastase, correctly describes the dissolution of the cell-walls of the endosperm during the germination of barley, but attributes this action to the agent which is instrumental in dissolving the starch. As he was able to extract from germinated barley small quantities of *formic acid*, and also found that this acid has the power of transforming starch into sugar, he came to the somewhat astonishing conclusion that the dissolution of both cellulose and starch in the natural grain is brought about by the direct action of the formic acid which is disengaged by the embryo.

This statement is entirely at variance with the results recorded in this paper, and is contradicted by the simple facts that the agents which are instrumental in dissolving the cellulose and starch have their hydrolytic activity paralysed by the mere action of heat, and that dilute formic acid has no action upon the ungelatinised starch-granule. It is, however, highly probable, from the results of our experiments, that the liberation of a small quantity of acid by the growing embryo, which certainly seems to occur, is instrumental in increasing the activity of the ferment-secreting cells, and in intensifying the hydrolytic activity of the enzymes after secretion.

From time to time, an occasional suggestion has been made that the changes in the endosperm may possibly be due to the action of *micro-organisms*, but, as far as we know, only one serious attempt has been made to prove the presence and multiplication of bacteria within the uninjured tissues of the seed. This was recorded in 1888 by H. Bernheim (*Chem. Zeitung*, No. 80), who attempted to show that bacteria play a prominent part in the germination of grain, and that they exist in the resting seed in the form of spores, increase under the influence of air and moisture, and are instrumental in producing diastase by the alteration of the reserve albuminoïds. It is further stated by this observer that he prepared pure cultures of various cocci and bacilli from the interior of maize and other grain.

During the progress of our work, we have frequently made very careful search in germinating grain for traces of bacteria, but have never found within the tissue of the endosperm a trace of these organisms, except under conditions which were favourable to their access from without. Our own observations on this point are in accord with those of Frankhauser (*loc. cit.*), and the recent critical examination of Bernheim's work by Buchner (*Münch. medizin.*

Wochenschrift, 1888, 906) sufficiently indicates the untrustworthiness of his conclusions.

There is still another possible explanation of the production of the large amount of amylo-hydrolytic enzyme during germination.

It has been shown by J. R. Green (*Phil. Trans.*, 178, 1887, B, 39) that germinating lupin seeds contain a proteo-hydrolytic ferment, which is capable of converting fibrin into peptone, leucin, and tyrosin. This ferment appears to exist in the resting seed, not in an active form but as a *zymogen*, the small amount of acid which arises during germination reacting on this zymogen, and developing from it a soluble ferment, under the action of which the transformation of the resting products readily takes place.

It did not seem at all improbable that some action similar to this might occur during the germination of the seeds of the Grasses, and that the small quantity of acid produced by the embryo might react upon a zymogen existing in the endosperm, and so produce from this mother-substance an active diastase.

This possibility has been carefully borne in mind during the course of our work, and we have already described the results, which were in all cases *negative*, of some experiments made upon the endosperms of barley with the particular object of producing an amylo-hydrolytic enzyme from the contents of their cells. It is true that the experiments of Reychler and of C. J. Lintner and Eckhardt have shown the possibility of preparing an amylo-hydrolytic enzyme from certain grain albuminoïds by long digestion with dilute acid, but the starch-transforming powers of the product are, as we have already seen, essentially different from those of the intensely active form of diastase which is found in the endosperm and in certain parts of the embryo during germination.

All the evidence points to the highly active form of amylo-hydrolytic enzyme being a direct glandular secretion of the columnar epithelium of the embryo, and we cannot explain its presence in the endosperm on any other assumption.

(21.) *The Form in which the Reserve Starch, after Transformation, enters the Growing Embryo, and a Consideration of the Metabolic Changes which it there undergoes.*

Since the starch-granules of barley are acted upon by a solution of the isolated "diastase of secretion" with all the phenomena of "pitting," &c., which attend their dissolution under the same agency within the natural endosperm, it is fair to assume that the actual chemical products of the reaction are the same in each case, *maltose* being the final result; and that this maltose suffers no further metabolic change within the dead and disintegrated tissue in which it arises, but is absorbed as such by the columnar epithelium of the scutellum. Fortunately, however, clear as it may seem, we are not left wholly to inference in this matter, as a considerable amount of direct chemical evidence is available, the sugars of some of the germinated and ungerminated cereals having been made the subject of more or less elaborate researches, which we must now consider.

The presence of cane-sugar in germinated barley was first demonstrated by Kühnemann in 1875 (*Ber.*, **8**, 202 and 387), and was subsequently confirmed by one of us and Heron four years later (Trans., **35**, 1879, 609) when it was shown that a cold aqueous infusion of malt contains a very appreciable quantity of cane-sugar, and that this cane-sugar, on digestion of the infusion, is inverted under the action of a special invertive enzyme, which also has its origin in the malt. In the year 1881, Kjeldahl (*Résumé du Compte rendu des travaux du Laboratoire de Carlsberg*, 1881, 189) published the results of a research upon the carbohydrates of barley and malt, with special reference to the presence therein of cane-sugar. The estimations of cane-sugar were effected by inverting the cold-water extracts of the malt with invertase, or with *yeast* in which the power of producing an alcoholic fermentation had been paralysed by means of thymol. The amount of cane-sugar was found by taking the increased cupric-reduction of the solution after inversion, and controlling by an observation of the loss in optical activity. The two methods gave results which were in close accord with each other, and the accuracy of the process was shown by its application to mixtures of carbohydrates containing known quantities of cane-sugar. The aqueous extracts of the grain upon which the determinations were effected were prepared in such a manner as to prevent any action of the natural invertive ferment of the malt. This was brought about either by employing a little sulphurous acid (which was subsequently removed with baryta) or by dehydration of the malt with absolute alcohol, and submitting it, in order to destroy the invertive ferment, to a temperature of 100° before extracting with water.

Whilst ungerminated barley contains only about 1·5 per cent. of cane-sugar, it was found that "green" malt (that is, malt ready for the kilning process) contains as much as 4·7 per cent., showing a decided increase during germination. No dextrin could be found in malt.

Kjeldahl endeavoured to estimate the *maltose* present in malt by a direct method, based upon an observation of one of us and Heron (*Proc. Roy. Soc.*, 1880, 393) that maltose is hydrolysed into dextrose by a ferment existing in the small intestine of animals. The results were not very concordant, but pointed to the existence of about 4 per cent. of maltose in barley-malt.

In 1886, O'Sullivan, without any knowledge of the work of Kjeldahl just alluded to, made a very careful examination of the sugars existing in ungerminated and germinated grain (Trans., 1886, **49**, 58). The method employed for a determination of the cane-sugar was substantially the same as that of Kjeldahl; the sugars were, however, extracted with alcohol instead of with water, and by the combination of a fermentation method with determinations of the optical and cupric-reducing powers of the solutions, certain valuable conclusions were arrived at with regard to the nature and amount of the other sugars present.

Ungerminated barley was found to contain 0·8 to 1·6 per cent. of cane-sugar, and a small but variable quantity of a sugar or sugars with a less reducing power than dextrose, and showing lævorotation. O'Sullivan gives no positive opinion as to what these sugars are, but the results suggest that *invert-sugar* constitutes a considerable proportion, and we must also include amongst them a small quantity of *raffinose*, which the same observer at a subsequent date (Trans., 1886, **49**, 70) proved to exist in barley.

As the result of a large number of examinations of barley-malt, O'Sullivan found the ready formed sugars to vary within the following limits:—

Cane-sugar........	2·8	per cent.	to	6·0	per cent.
Maltose	1·3	,,	,,	5·0	,,
Dextrose..........	1·5	,,	,,	3·0	,,
Levulose..........	0·7	,,	,,	1·5	,,

These experiments clearly indicate a large increase in the cane-sugar during germination, and a production of maltose, dextrose, and levulose. O'Sullivan concludes that the *maltose* is derived from the starch, which unquestionably disappears during germination, but he gives no opinion as to the origin of the cane-sugar and its products of inversion.

Before considering more fully the origin and distribution of the sugars of germinated grain, it will be well to give actual chemical proof of the disappearance of starch during germination, a fact which is abundantly evidenced by the micro-chemical observations to which we have so frequently alluded. We give below determinations of the actual quantity of starch in a given number of grains of barley before and after germination, the amount of starch being expressed in each case in actual weights. The estimations were made by the method recommended by O'Sullivan (Trans., 1884, **45**, 1), which consists essentially in hydrolysing the starch by diastase, and determining the amount as maltose and dextrin.

Starch in 1000 *Corns.*

	Starch in barley before germination. grams.	Starch in barley after six days' germination. grams.	Loss of starch in grams.
Expt. (1)	20·0552	15·4398	4·6154
„ (2)	19·9158	15·3636	4·5522

It is manifest that a determination of the total amount of sugars diffused throughout the germinated grain cannot teach us much with regard to their origin, but that considerable light may be thrown upon this point by ascertaining the relative distribution of the sugars between the embryo and endosperm. With this end in view, we have dissected out the embryos from a large number of grains of barley before and during germination, and have determined the nature and amount of the sugars after separate extraction of the embryos and endosperms with alcohol. We used substantially the same method as O'Sullivan,* determining in each case the cane-sugar by invertase, the nature of the other sugars being inferred from a consideration of their optical and cupric-reducing properties. The results indicate that the sugars consist almost entirely of cane-sugar, invert-sugar, and maltose.

In the first table we have expressed the results, for purposes of comparison, not in percentages but in actual weights of each sugar obtained from a given number of grains of barley before and after germination.

Sugars in 250 *Corns of the Barley.*

	Barley, after steeping in water for 48 hours.		Barley after germination for 10 days.	
	Embryos.	Endosperms.	Embryos.	Endosperms.
	grams.	grams.	grams.	grams.
Cane-sugar	0·0204	0·0338	0·3430	0·1787
Invert-sugar	0·0070	0·0227	0·0174	0·1790
Maltose	—	—	—	0·3640
Total sugars	0·0274	0·0565	0·3604	0·7217

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* The finely divided tissue was first treated with ether in a Soxhlet's extractor in order to take out the fat, and the sugars were afterwards extracted with alcohol in the same apparatus.

The following table represents the quantities of the various sugars, expressed in percentages on the dry weights of the 250 embryos and endosperms respectively.

	Barley after steeping in water for 48 hours.*		Barley after germination for 10 days.	
	Embryos.	Endosperms.	Embryos.	Endosperms.
	per cent.	per cent.	per cent.	per cent.
Cane-sugar............	5·4	0·3	24·2	2·2
Invert-sugar	1 8	0·2	1·2	2·2
Maltose	—	—	—	4·5
Total...............	7·2	0·5	25·4	8·9

The results given in the table illustrate in a very striking manner the increase of sugars during germination (an increase which we have seen is accompanied by a diminution in the starch), and the very marked differences which exist in their relative distribution between embryo and endosperm. We see that whilst in the germinating seed the presence of *maltose* is confined to the *endosperm*, the part of the grain in which it takes its origin, the greater part of the *cane-sugar*, on the other hand, is found in the growing *embryo*, whose tissues are excessively rich in it, for it amounts to nearly 25 per cent. of their dry weight.

We cannot avoid the conclusion that transformed starch is absorbed from the endosperm by the columnar epithelium of the embryo in the form of *maltose*, and that this maltose, by the more or less complicated metabolic processes of the living cells of the embryo is rapidly converted into *cane-sugar*. The small percentage of cane- and invert-sugar in the endosperm is probably accounted for by diffusion from the plumule across the very thin dividing tissue of the endocarp and testa. Such a diffusion must certainly take place during the alternate moistening and partial drying to which the grain was subjected during germination.

We have been able to demonstrate in a very striking manner the ability of the growing tissue of the embryo to convert maltose into cane-sugar. This was done by cultivating the excised embryos of barley upon a solution of maltose, and determining the cane-sugar in the plantlets after such cultivation. Although under these circumstances cane-sugar may be found within the embryo, not a trace can be discovered in the culture-medium itself, which we should expect if the maltose were converted by the action of any secreted ferment.

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* The small amount of sugars in the ungerminated barley, as compared with the results of Kjeldahl and O'Sullivan, is due to the long steeping of the grain previous to analysis. The germinated and ungerminated samples were treated in the same manner in this respect, to ensure a proper comparison of the results.

When, on the other hand, embryos are grown upon solutions of *dextrose* instead of maltose, it will be noticed that no cane-sugar is formed in their tissues, but that the reducing sugars present in each case have optical and reducing properties corresponding to a mixture of invert sugar and dextrose.

Sugars present in 250 *Barley Embryos after six days' Culture on* (1) 3·5 *per cent.* maltose *solution;* (2) 3·5 *per cent.* dextrose *solution.*

	(1.) Maltose solution. grams.	(2.) Dextrose solution. grams.
Cane-sugar	0·113	—
Dextrose	0·042	0·018
Invert-sugar	0·081	0·162
Total sugars	0·236	0·180

The constant presence of large quantities of cane-sugar in the embryo of barley when growing under natural conditions, that is, attached to its endosperm, explains to some extent the high nutrient value of this sugar as compared with other carbohydrates, in artificial culture experiments with the excised embryos. Its superiority in this respect over the natural nutritive carbohydrate maltose can be understood if we bear in mind that the maltose has to be first converted into cane-sugar, and that this expenditure of energy on the part of the living cell is rendered unnecessary if the nutrient substance is given in the shape of ready-formed cane-sugar.*

The intimate connection between cane-sugar and starch in plants has been clearly shown of late years by several chemists. In the case of the tuber of the potato, the dependence of its reserve starch upon the previous existence of cane-sugar in the juices of the plant has been very well shown by Aimé Girard (*Compt. rend.*, **108** (1889), 602). The same has been done for *maize* by H. Lepley (*Compt. rend.*, **94** (1882), 1033), and for *wheat* by Balland (*Compt. rend.*, **106** (1888), 1610).

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* The necessity which the growing tissue is under of having to convert the absorbed maltose into cane-sugar before it can be passed on from cell to cell is paralleled by a somewhat similar phenomenon in the animal organism. Under the influence of the amylo-hydrolytic enzymes of the pancreas and small intestine, as was shown by one of us and Heron in 1880 (*Proc. Roy. Soc.*, 1880, 393), starch is rapidly converted into maltose, but we have good reasons for believing that on absorption by the epithelium of the small intestine it is further converted into *dextrose*, in which form it enters the portal blood, and is subsequently made use of by the animal organism. The correctness of this view has been rendered still more probable by the subsequent researches of S. J. Phillips (Maly's *Jahresb. der Thier. Chem.*, 1881, 60).

In a series of experiments which we conducted a few years ago upon the barley plant, taken from the fields at various stages of its growth, we were able to satisfy ourselves that cane-sugar forms a large proportion of the sugars existing in the sap of the plant, and that this cane-sugar disappears *pari passu* with the formation and accumulation of starch in the seed.

It is doubtless in the form of cane-sugar and its products of inversion that the transference of carbohydrates in the Grasses mainly takes place. That this translocation or wandering of the sugars is brought about to some extent by the ordinary physical processes of osmosis is in the highest degree probable, but we must always bear in mind that the living cells behave in respect to diffusible substances very differently from artificial septa, or from the same cells after their vitality is destroyed. Although it is possible to have a ready exchange of water between the cell-sap of the vacuole and a solution of a diffusible substance placed outside the primordial utricle, yet the protoplasm itself, as long as it is living, constitutes a most formidable barrier to the passage, outwards or inwards, of even the most diffusible substances.

The scutellum of the Grasses affords a good subject for investigations of this nature, for we have seen that all the nutrient substances derived from the endosperm must pass through its tissues on their way to the growing parts of the plant.

The cell-walls of the parenchyma and the intercellular spaces afford means for the sugars to pass through this tissue by processes of diffusion, but if these were the ordinary channels made use of by the soluble carbohydrates, we should expect to find a considerable quantity of *maltose* in the growing embryo, unless indeed the conversion of maltose into cane-sugar takes place during the passage of the former across the single row of cells forming the absorptive epithelium.

That the nutritive carbohydrates really gain access to the cell-protoplasm is shown by the abundant formation of transitory starch within it, and it has been suggested by Sachs that the wandering of the sugars across the parenchyma is brought about by the successive formation and dissolution of this transitory starch, which is thus in a constant state of flux. If this view is correct, we have still the same difficulty in explaining how the products of dissolution of the transitory starch pass on from cell to cell.

It seems to us far more probable that after the maltose has passed through the absorptive epithelium it diffuses through the cell-walls of the parenchyma to the primordial utricle, and is then incorporated with the protoplasm, from which the cane-sugar is subsequently elaborated. The sucrose, which is in excess of the amount demanded by the cell for carrying on its processes of constructive and destructive metabolism, is temporarily accumulated as such in the cell-sap, or as transitory starch in the protoplasm itself. In the actual passage of material from cell to cell the continuity of the protoplasm doubtless plays a most important part.

We are continuing our experiments on the germination of the Grasses, and are engaged in applying the methods we have described to an elucidation of the changes which other reserve materials, more especially the proteïds, undergo in their passage from the endosperm to the embryo, and of the agencies which are at work in bringing about their transformation.

(22.) *ADDENDUM. A Consideration of the Recent Hypothesis of G. Haberlandt, that the Aleurone-Layer Secretes Diastase.*

We have already (p. 473) briefly alluded to the suggestions which have been made from time to time that the aleurone-layer of the endosperm of the Grasses is in some way or other intimately connected with the production of diastase during germination, and we have also stated that our experiments, as far as they go in this direction, are opposed to the correctness of this view.

We had intended to discuss fully the evidence upon which this opinion was based in a subsequent part of our paper, but have considered it desirable to do so at once, owing to the recent publication of an important memoir having a direct bearing on this subject.

A few days after the foregoing portion of this communication had been sent in to the Chemical Society, there appeared in the *Berichte der deut. botanischen Gesellschaft*, 8, 40, a paper by G. Haberlandt, entitled "Die Kleberschicht des Gras-Endospermes als Diastase ausscheidendes Drüsengewebe," in which the author attempts to show that the aleurone-layer does not belong entirely to the reserve-system of the seed, but that during germination the cells composing this layer function as a glandular tissue, and secrete diastase into the adjacent starch-containing portion of the endosperm. The experiments described were performed upon *rye*, but the author considers that the aleurone-layer in all the Grasses functions in a similar manner.

After noting the microscopical appearance of the aleurone-cells and their contents in the resting stage of the seed, and drawing attention to Tangl's proof of the continuity of the protoplasm through the cell-walls, Haberlandt describes certain changes which occur in the cells during germination, and which appear to indicate that the protoplasm is still living, and is capable of availing itself of the plastic structural materials stored up within it.

A determination of the progress of the dissolution of the endosperm starch during germination was made by cutting out and examining small pieces of the starch-containing tissue, almost exactly in the manner we have described in the case of our own experiments. It is stated that corrosion of the starch-granules first occurs between the scutellum and the aleurone-layer on the ventral side, and that this action rapidly extends to the starch-granules adjacent to the dorsal side of the scutellum, and from these facts it is concluded that the embryo actually secretes diastase. As germination proceeds and the action upon the starch gradually extends, this is found to take place much earlier in the cells of the endosperm lying immediately under the aleurone-layer than in those of the central portions of the endosperm, and it was observed that dissolution of the starch on the ventral side, in the neighbourhood of the "furrow," took place last of all. This mode in which the diastatic action progresses suggested to Haberlandt that not only the scutellum, but also the aleurone-layer, might have the power of secreting diastase.

Certain direct experiments were then made with a view to test the truth of this supposition. When germination has proceeded sufficiently far, the connecting tissue between the starch-bearing portion of the endosperm and its aleurone-layer is broken down, and the latter then remains in close connection with the testa and pericarp.

Pieces of the integument, including the aleurone-layer, were cut out from rye which had been germinated to the above point, and after washing these with a brush wetted with a sugar solution of 1 to 2 per cent., in order to free them as much as possible from the adherent corroded starch-granules, they were placed upon moist filter-paper with the aleurone-layer upwards. Upon the aleurone-layer there was placed, with the aid of a brush, a small quantity of moistened rye-meal, or of starch mixed with water, and the whole was kept moist and submitted to a temperature of 18—20° C.

Within 24 hours, corrosion of the starch-granules was found to have taken place, and as no such corrosion could be observed in starch placed alongside on the filter-paper for purposes of control, it is concluded by Haberlandt that the action upon the starch can only have been brought about by a diastatic ferment secreted by the aleurone-layer.

Having settled this point to his satisfaction, the author then asks himself the question whether the aleurone-cells generate the enzyme, or whether they merely act, according to Tangl's views, as carriers of diastase from the embryo. In order to throw some light upon this point, the continuity of the aleurone-layer was broken in some corns before germination by cutting round the edge of the scutellum, and so "ringing" the aleurone-layer, exactly in the same manner as we have done in certain similar experiments, described in the text of our paper. Haberlandt found, just as we did in similar cases, that notwithstanding this break in the continuity of the aleurone-layer, and its complete severance from the embryo, the spread of the diastatic action in the mutilated corns, when these were subsequently germinated, took place in the usual manner, and the integuments with their adherent aleurone-layer had all the power of corroding starch when this was placed in contact with the aleurone-cells, as described above.

From these facts Haberlandt draws the conclusion that diastase is secreted by the aleurone-cells, and that it is formed during germination within these cells, which function in a manner similar to the digestive glands of insectivorous plants.

The resting aleurone-layer contains no appreciable amount of diastase, for when corns of rye, deprived of their embryos, were placed under conditions favourable for germination, no evidence could be obtained of any diastatic action upon the starch immediately under the aleurone-layer, although the aleurone-cells had undergone all the histological changes which are observed in the same cells in uninjured and germinating corns, when they are apparently actively secreting. Haberlandt remarks upon this as being somewhat extraordinary, but states that he has observed much the same thing with regard to the secretion of diastase by the scutellum; that if the embryo is so far removed as to leave only the scutellum attached to the endosperm, no subsequent action upon the starch takes place, but that if only one lateral root was left attached to the scutellum, a certain amount of action takes place on the starch. From this it follows, according to Haberlandt, that the commencement of the formation of the diastatic enzyme and its secretion are closely connected, both on the part of the aleurone-layer and of the scutellum, with the presence of a germ capable of development, and that it is metabolism of the growing germ which gives the start to the production of diastase in these organs. When this action has once commenced, isolated parts of the aleurone-layer can continue the secretion of the enzyme for a considerable time.

These are the principal facts recorded by Haberlandt in support of his views, and we must now submit them to a critical examination in the light of our own experiments.

At a comparatively early stage of our inquiry into the rate of progression of the dissolution of the endosperm-starch during germination, we noticed, just as Haberlandt has done, that progress of the action takes place more readily in certain definite directions than in others, the rate of this progress being more rapid in the peripheral portions of the dorsal side of the grain, immediately under the aleurone-layer. To this fact we have drawn special attention in our paper, and have attempted to depict it in diagrammatic form in Plate 2 (p. 468).

We were at first inclined to believe, as Haberlandt does, that this peculiarity in the progress of the action upon the starch was due to some special influence of the aleurone-cells, and we made many unsuccessful endeavours to obtain evidence of direct diastatic action of these cells upon the underlying starch of the endosperm. We found that the action upon the starch invariably progressed in an unbroken zone from the scutellum in a distal direction, and that no evidence could be obtained of any action taking place upon isolated portions of the periphery of the endosperm, which one would expect to occur if the starch were acted upon by a secretion of diastase from the aleurone-cells.

This constant and well-marked progression of the starch-dissolving action received its true explanation when we came to recognise the important fact that dissolution of the cell-walls of the starch-containing endosperm tissue is a necessary preliminary to dissolution of the contained starch. The question really resolves itself into determining why the cell-walls of the endosperm give way to the solvent action of the cellulose-dissolving enzyme more readily in certain definite directions, for it is quite certain that the diastatic enzyme, with its low rate of diffusibility, will follow in the path marked out for it by the cyto-hydrolyst.

We have not in this case to fall back upon any supposed action of the aleurone-cells upon the cell-walls of the underlying tissue, for, as we have already noted in the body of the paper, when thick or thin transverse sections of barley, even after previous treatment with alcohol, are immersed in a solution of the cyto-hydrolytic enzyme, or in malt-extract made from air-dried malt, the cell-walls of the starch-containing cells situated peripherally on the dorsal half of the sections show a very much smaller resistance to the action of the enzyme than do the cell-walls of the central portions, or of the peripheral portions of the ventral side, especially in the neighbourhood of the furrow. The varying resistance of the cell-walls and the progress of their dissolution can be watched under the microscope if thin transverse sections of barley are immersed in "hanging drops" of the cyto-hydrolytic ferment, and it can be distinctly shown that those parts of the endosperm in which action upon the starch progresses most rapidly during ordinary germination are those which afford least resistance to the cellulose-dissolving enzyme. That the starch is more quickly acted upon during germination immediately under the aleurone-layer of certain portions of the grain, is due, not necessarily to any direct action of the aleurone-cells, but to the fact that the cell-walls in this part of the endosperm are younger, and break down more readily in consequence.

We must now turn to the direct experiments upon which Haberlandt relies for proof that the aleurone-cells possess a secretory power. It will be remembered that his principal experiment consists in separating the aleurone-layer, still adherent to the testa and pericarp, from a grain of rye which has been so far germinated as to have its starchy endosperm completely disintegrated. After washing the inner aleurone-layer with a brush dipped in a weak solution of sugar, it was found to possess the power of corroding starch within a comparatively short time.

We have repeated this experiment many times with germinating barley, taking the precaution to wash the sections copiously with water, instead of with a solution of sugar, which might exercise an inhibitory effect on the secretion. The fragments so treated were placed, aleurone-layer downwards, on a very thin layer of barley-starch spread upon moistened filter-paper, and we invariably found a very considerable amount of action on the starch within 24 hours.

So far the observed facts are entirely in accordance with those noted by Haberlandt, but it by no means follows that the action on the starch is due to the secretory power of any portion of the fragment. We must bear in mind that the aleurone-layer and the integuments have been in most close and intimate contact with a portion of the endosperm which, at the stage of growth at which the dissection was made, was highly charged with accumulated diastase, and it would be strange indeed if the tissues of the aleurone-layer and of the integuments did not retain, especially in their intercellular spaces, some of the enzyme, which it would be very difficult to remove even by long-continued washing, and quite impossible to remove by a mere brushing with a moistened camel's hair pencil.

In our endeavours to ascertain if this experiment of Haberlandt really affords any positive evidence of secretion of diastase by the aleurone-cells, we have availed ourselves of the methods which we employed whilst investigating the secretory powers of the scutellar epithelium. It will be remembered that fresh tangential sections of the scutellum, including any portion of the epithelium, were found to secrete diastase, and to readily act upon starch-granules placed in contact with them, but that the sections lost all such power if the epithelial cells were previously killed by being submitted for a short time to the vapour of chloroform. When portions of the integuments of germinating barley with their adherent aleurone-layer are treated in a similar way with chloroform vapour, we have found that their diastatic power *is not in the least impaired*, the starch under such sections being as quickly and completely attacked as that under sections which have received no such treatment.

Moreover, we have observed exactly the same thing even *after the fragments have been immersed for some time in absolute alcohol.* This treatment must have infallibly destroyed any vitality which the aleurone-layer possessed, yet, on careful comparison, we find the sections as diastatically active as before immersion in the alcohol. The experiment of Haberlandt becomes then valueless as a direct proof of the secretory power of the aleurone-layer. The aleurone-cells may, it is true, possess some such secretory functions, but this is not in any way proved by the experiment, as the diastatic action takes place whether the aleurone-cells are living or dead, and the phenomena can be equally well explained by the adherence of diastase to the sections, the enzyme having been derived from the main portion of the endosperm with which they were originally in contact.

If the aleurone-cells possess any such power of secretion as has been ascribed to them, it certainly ought to be possible to obtain some evidence of this by separating the aleurone-layer of the resting seed and placing it under conditions favourable to the revival of the dormant activity of its constituent cells.

During the earlier part of last year, we made many experiments with this object in view, and since reading Haberlandt's paper have repeated them many times, but always with negative results.

From barley, previously soaked in water, or in some cases from the dry corn without any preliminary treatment, the paleæ are removed, and thin sections of the grain are made tangential to the surface of the pericarp. If the sections are prepared in such a manner as to include in their thickest or central parts a trace of the starch-containing cells, it is easy, owing to the triple arrangement of the aleurone-layer, to ensure the presence in the sections of a large number of the uninjured aleurone-cells. When these cells are brought into intimate contact with moistened barley-starch spread upon filter-paper, most careful observations have always failed to detect any action on the starch which can in any way be directly attributed to the secretory powers of any cells composing the sections. If we place alongside, for purposes of comparison, thin tangential sections of the *scutellum*, with their epithelium in contact with the starch, the contrast is very remarkable when these are watched from day to day. In less than 24 hours, the starch-granules under the scutellum sections are visibly acted upon, and this action increases rapidly in intensity until, within three days, every starch-granule within a short distance of the section is either dissolved or enormously eroded. On the other hand, not the slightest change can be detected in the starch-granules underlying the tangential sections of the aleurone-layers for at least five or six days. At the end of that time, it is generally possible, by searching examination, to detect here and there a granule showing incipient signs of corrosion, but these are extremely few in number, and since an equal number of slightly-eroded granules can be detected under sections of the *paleæ*, placed alongside for purposes of comparison, it is clear that the slight action observed at the fifth or sixth day is due to the influence of the micro-organisms which now abound in the neighbourhood of all the sections.

The results obtained by putting similar sections of the scutellum and of the aleurone-layers upon stiff *starch-paste* are, perhaps, even more striking. The tangential sections cut from the centre of the *scutellum*, and placed, epithelium downwards upon the starch-paste, within 12 to 15 hours of the commencement of the experiment liquefy the starch-paste by means of the secreted diastase, and gradually sink into the liquid, whilst the sections including the *aleurone-layers* at the end of three days *fail to produce any liquefaction of the starch-paste.*

Haberlandt has himself drawn attention to the fact that, after removing the embryo from the rye and placing the germless endosperm under conditions favourable for germination, no sign of action can be observed in the starch immediately underlying the aleurone-layer, and yet the histological changes which take place in the aleurone-cells under these conditions do not differ from those observed in germinating grain at a time when he considers them to be actively secreting. This fact in itself is sufficient to throw considerable doubt upon the accuracy of the secretory hypothesis as regards these cells. If we are to accept Haberlandt's explanation of this fact, we must assume that the presence of a germ capable of development has some mysterious power of influencing the aleurone-cells across the intermediate dead tissue of the starch-containing portion of the endosperm, and of so far controlling their metabolic processes as to cause active secretion of a special enzyme. That this influence, if it exists, must be exerted across this neutral tract is clear, for the results of the experiments on "ringing" the aleurone-layer, as carried out both by Haberlandt and ourselves, negative the idea that this supposed influence can be transmitted from the germ through the portion of the aleurone-layer lying in intimate contact with it at the proximal end of the seed. The difficulty in rightly understanding this supposed influence of the growing embryo appears also to have struck Haberlandt, who, however, instances, as another case of this kind, a supposed similar influence of the growing embryo upon the secretory functions of the scutellum. It is certainly not correct, however, to say that the secretory function of the scutellum is necessarily dependent upon the growth and metabolism of any of the main axial organs, for our experiments abundantly prove that a portion of the scutellum itself, no matter how small it may be, providing it still has its epithelium attached, will, under favourable conditions, secrete diastase and act upon starch.

But we have not yet exhausted all the experimental evidence which we have obtained whilst attempting to verify the alleged secretion of diastase by the aleurone-cells.

If Haberlandt is correct in his idea that the aleurone-cells require some stimulus from the growing embryo to initiate their secretion, and that the action, having been once established, may continue for some time in isolated portions of the aleurone-layer, it follows that if we remove the embryos from corns which are already in an advanced state of germination, there ought to be a sensible accumulation of enzyme in the endosperm for some time after the separation of the germ. The methods which we have described for the determination of diastase in germinating grain fortunately allow us to put this to the test of experiment. After germinating some barley for five days, the embryos were excised from 100 corns, and the endosperms were treated as follows:—

In Experiment A, the diastase was determined at once in 50 of the endosperms.

In Experiment B, the remaining 50 endosperms were maintained at ordinary temperatures in a moist atmosphere for two days longer, and the diastase determined in them at the end of that time.

Experiment A. Diastase equivalent to 19·235 grams CuO.
" B. " " 13·910 "

In the endosperms of 50 corns which had been allowed to germinate *in the unmutilated state* for seven days, diastase was found equivalent to 21·890 grams CuO.

Instead of there being any increase in the amount of diastase in the endosperm of germinating barley after the removal of the embryo, as we should reasonably expect if Haberlandt's ideas are correct, we find *a marked decrease* in the amount of enzyme. It is natural to expect that there would be a diminution in the amount of diastase due to its continued action upon the starch, and it is very evident that either there is no secretion of diastase at all by the aleurone-cells, or that the amount of secretion is not sufficient to take the place of the enzyme which has been exhausted in hydrolysing the starch. On the other hand, in the corns to which the embryos were still attached, there was a marked increase and accumulation of enzyme within the same time. This experiment certainly does not countenance the view that the aleurone-cells are capable of secreting diastase to an extent at all comparable with the secretion effected by the scutellum.

As far as the evidence goes at present, we are certainly not justified even in suspecting that the cells of the aleurone-layer are glandular in the same sense as are the epithelial cells of the scutellum, and until evidence of a far more convincing nature is forthcoming, we must adhere to the opinion that the diastase accumulated in the germinating seeds of the Grasses owes its origin exclusively to the secretory glandular cells forming this scutellar epithelium, and that the aleurone-cells belong solely to the reserve-system of the seed.

Burton-on-Trent.

XXXI.—*The Terminology of Hydrolysis, especially as affected by "Ferments."*

By Henry E. Armstrong.

All who consider the meaning of words and who desire, as far as possible, to remove ambiguity from the terms employed in denoting chemical change must have felt some dissatisfaction with the nomenclature used, chiefly by physiologists, in describing and discussing the remarkable phenomena presented by the living cell and which attend digestion. As the authors of the previous paper "*On the Germination of the Gramineæ*" have done me the honour to accept several of my suggestions, I venture to regard the opportunity as one which should not be lost of discussing the terminology of fermentation phenomena.

Changes such as a glucose undergoes when it is resolved into carbon dioxide and ethyl alcohol take place under the influence of the living organism, and there is every reason to believe only *within* the cell: they involve the formation of products containing in the gross neither more nor less than the original elements of the compound fermented; and when the products are compared with the compound from which they are derived, it is seen that their production in all cases involves the separation of carbon atoms which were directly united, and also considerable rearrangement of the constituent elements.

Changes such as that which cane-sugar undergoes on inversion take place not only within the cell but equally well without it under the influence of a substance which, although not living, is of vital origin: they appear always to involve the fixation of the elements of water; and the products of their action bear a very simple relation to the original substance, viz., always that of an alcohol to its ether, no separation of directly-united carbon-atoms, or any molecular rearrangement such as attends the former class of actions, taking place. The agents derived from organisms which effect changes of this second kind are spoken of as *unorganised ferments;* changes of the first kind are said to be conditioned by *organised ferments*, *i.e.*, *organisms.*

There is thus, at the outset, a difficulty in assigning a consistent meaning to either term—fermentation or ferment: diverse phenomena produced by diverse agents being included under a single designation.

Fermentation.—The difficulty is in part met by restricting the term fermentation to changes such as occur, for example, during alcoholic fermentation; and there would seem to be no occasion to apply it more widely so as to include changes of the second kind, these, as before remarked, being apparently all cases of *simple hydrolysis.* This is true, even if the explanation of fermentation suggested by Baeyer in 1870 (*cf. Ber.*, 1870, 63; this Journal, 1871, 331) be accepted, which represents fermentation proper as the outcome of hydrolysis—an explanation which the increase of knowledge in the interval entirely favours: inasmuch as hydrolysis takes place in the two cases with different results and affects compounds of different types. Moreover, it is to be noted that not only is it impossible to represent the phenomena of fermentation proper as the outcome of simple hydrolysis, but that also, in certain cases, synthetic as well as analytic changes occur: in the case of butyric fermentation, for example. In fact, in many instances, apparently two series of concurrent changes take place: the one series involving what, in the light of Baeyer's explanation, may be termed *recurrent* as distinguished from *simple* hydrolysis; the other involving the interaction of the molecules of one or more products of this recurrent hydrolysis. There is thus an advantage in employing a somewhat empirical expression in connoting phenomena which do not all conform to one absolute type, but which have a common origin, as they are the outcome of protoplasmic activity, especially as most fermentations are attended with evolution of gas.

But it is to be remembered that whereas carbohydrates and allied compounds such as glycerol, lactic acid, &c., are said to undergo *fermentation*, the decomposition of albuminoids under the influence of organisms is commonly termed *putrefaction;* this distinction, however, is made on account of the character of the products, not because there is any reason to suppose that the changes which occur are essentially different in character from those which the carbohydrates undergo. The want of a term indicative of the fact that the action is one which takes place under vital influence without reference to the character of the change—equally applicable to simplifications such as occur during alcoholic fermentation and to complications such as occur during butyric fermentation—is also felt in the case of changes such as alcohol undergoes under the influence of *Mycoderma aceti* and *vini*, or which ammonia undergoes on nitrification, and in the converse change of denitrification. Dr. W. Roberts has proposed to speak of changes induced by enzymes (*v. infra*) as cases of *enzymosis;* the corresponding term *zymosis* might well be employed as the synonym of fermentation, and would probably be found to be of more general application: thus alcohol may be said to undergo oxidation by zymosis or zymic oxidation under the influence of *Mycoderma aceti;* and in discussing putrefactive changes, it would be possible to speak of zymic changes as distinct from those arising from the unassisted interaction of the zymic products. Zymosis is preferable to *zymolysis*, as the effect is not always one of simplification.

Ferments.—The expression *ferment* is more frequently than not employed as the equivalent of *unorganised ferment;* consequently it is applied to the very agents which are incapable of producing fermentation proper. This has been so generally felt to be the case that several words have been coined in place of unorganised ferment, notably *zymase* and *enzyme* (*cf.* Dr. W. Roberts, *Roy. Soc. Proc.*, 1881, **31**, 145): the objection may be made to the former that it is indicative of vitality; the latter, however, is expressive, and serves only to indicate the vital origin of the agent, thus differentiating it from agents such as the mineral acids which act very similarly.

Enzymic action or enzymosis*—to use the phrase suggested by Dr. Roberts—appears, as already remarked, always to involve decomposition by means of water. On this account, in 1880, in the second edition of my "*Introduction to the Study of Organic Chemistry*" (Longmans. Footnote, p. 190) I put forward the following suggestions:—

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* Sheridan Lea's zymolysis (*cf. Journal of Physiology*, 1890, 11, 254) is open to the objection above made to zymase.

"Decompositions like those of starch into dextrose, of cane-sugar into dextrose and lævulose, of the fats into glycerine and an acid, or of ordinary ether into ethylic alcohol, which involve the fixation of the elements of water, may all be said to be the result of *hydrolysis;* and those substances which, like sulphuric acid, diastase, emulsin, &c., induce hydrolysis may be termed hydrolytic agents or *hydrolysts.* The substance hydrolysed is the *hydrolyte.* The mere fixation of the elements of water unaccompanied by decomposition, as in the conversion of ethylenic oxide into glycol, $C_2H_4O + OH_2 = C_2H_4(OH)_2$, may be termed hydration in contradistinction."

It is usually necessary to employ a specific enzyme (hydrolyst), or one of a very limited number, to effect the hydrolysis of any particular hydrolyte, and hence physiologists are in the habit of speaking of *amylolytic* ferments, *proteolytic* ferments, &c., meaning ferments capable of *splitting up* starch, proteids, &c. But the terms amylolytic, proteolytic, &c., are confusing to the student who has learnt that electrolysis signifies splitting up *by means of* electricity, and hydrolysis splitting up *by means of* water—not the splitting up *of* electricity or *of* water. As electrolysis and even hydrolysis are well-established terms which it would scarcely be politic to alter, it appears highly desirable to abandon the use of terms such as amylolytic, proteolytic, &c., and I would suggest that an enzyme capable of inducing the hydrolysis of starch should be termed an *amylo-hydrolyst;* one which affects albuminoids, a *proteid-hydrolyst;* one which affects fats, a *glyceride-hydrolyst.*

One case remains in which the use of the term ferment cannot be avoided by the adoption of this proposition—that of the so-called rennet ferment. It may well be that this is also a hydrolyst, and that in all cases the formation of a curd, clot or coagulum initially involves hydrolysis—or, perhaps, hydration merely—and the consequent interaction of molecules of the product or products; but of this we know nothing at present, and the observed phenomena are of so different a character that it is desirable to connote such changes by a distinct expression. I would suggest that we should term the rennets *thrombogenic enzymes* or *thrombogens.*

XXXII.—*Action of Phosphoric Anhydride on Fatty Acids.* Part I.

By F. Stanley Kipping, Ph.D., D.Sc.

At a moderately high temperature, some fatty acids are decomposed by phosphoric anhydride with evolution of carbonic anhydride and formation of a ketone. This reaction may be represented by the equation—

$$2R{\cdot}COOH = R_2CO + CO_2 + H_2O.$$

Normal heptylic and stearic acids are the only compounds which have yet been systematically investigated in this direction, and in both cases a considerable quantity of the ketone is formed.

The only methods of any general application at present employed for the preparation of fatty ketones of the formula R_2CO are, as is well known, (1) by the distillation of the calcium or barium salts of the fatty acids, and (2) by the action of acid chlorides on the zinc compounds of the alcohol radicles.

The first of these methods cannot be considered satisfactory as regards either the quantity or the purity of the ketone obtained. By the distillation of calcium acetate, for example, Fittig found that not only acetone, but also the homologous ketones of the composition C_4H_8O and $C_5H_{10}O$ were formed, whilst calcium butyrate gives, in addition to butyrone, the homologues $C_5H_{10}O$, $C_6H_{12}O$, $C_8H_{16}O$, and $C_{11}H_{22}O$ (Limpricht, *Annalen*, **108**, 183; and Friedel, *ibid.*, 122); in both cases, therefore, the purification of the principal product would be a tedious and difficult process.

The other general method for the preparation of ketones is also an unsatisfactory one; it is troublesome to carry out and the materials employed are both expensive and difficult to prepare.

The experiments described below seem to show that ketones, or at any rate the higher members of the series, can be easily prepared by treating the fatty acids with phosphoric anhydride under suitable conditions. In the case of heptylic acid, two experiments, carried out under different conditions, gave 33 and 25 per cent. respectively of the theoretical quantity of pure dihexyl ketone, $(C_6H_{13})_2CO$, whilst with stearic acid the yield of pure stearone, $(C_{17}H_{35})_2CO$, is at least 40—42 per cent. of the theoretical; further experiments have yet to be made, in order to ascertain the conditions which give the best yield of the desired product.

In both reactions considerable quantities of other products are formed, but these are of such a nature that no difficulty whatever is experienced in isolating the ketones and obtaining them in a pure condition.

Experiments have already been commenced on the action of phosphoric anhydride on other acids, both of the fatty and aromatic series; their behaviour with zinc chloride and other dehydrating agents is also being investigated.

Preparation of Dihexyl Ketone, $(C_6H_{13})_2CO$.

Several experiments have been made with normal heptylic acid at temperatures varying from 140° to 220°, and with different quantities of phosphoric anhydride, in order to ascertain the most suitable conditions for the preparation of dihexyl ketone; the best results were obtained in the following manner:—10 grams of anhydrous heptylic acid are heated at 180° in a small flask placed in a metal- or oil-bath, and 6·5 grams of phosphoric anhydride is quickly added in three portions, the mixture being stirred well during the process; at first a considerable quantity of carbonic anhydride is evolved, and the temperature rises 10° or 15°, but the reaction is quickly at an end, the whole operation requiring only about three minutes. The flask is then taken out of the bath, allowed to cool, and the dark-brown mass gradually stirred up with water; the fact that there is little or no development of heat shows that the whole of the phosphoric anhydride has been changed, even when, as in this experiment, a quantity considerably in excess of the theoretical is employed.

The solution is now rendered strongly alkaline with potash or soda, and the contents of the flask transferred to a larger flask and distilled with steam; the ketone collects in the receiver in the form of a yellowish oil which, on cooling, solidifies to almost colourless, waxy plates. The crystalline substance is separated by filtration, allowed to dry in the air for a short time, and then spread on a porous plate to free it from traces of oily impurities.

It is thus obtained in an almost pure condition in colourless crystals melting at 28—30°.

1·4 grams of dihexyl ketone are obtained in this way from 10 grams of heptylic acid, but a considerable quantity of unchanged acid remains as sodium or potassium salt in the alkaline residues from which the ketone has been distilled. In order to isolate this acid, the alkaline solution is strongly acidified with dilute sulphuric acid and again distilled with steam; the aqueous distillate is extracted twice with ether, the ethereal solution dried over calcium chloride, and the ether evaporated. The heptylic acid (4 grams) which is thus obtained is almost pure, as shown by its behaviour on distillation, and can be directly employed for another operation.

Since, then, 6 grams of heptylic acid give 1·4 grams of dihexyl ketone, the yield is 33 per cent. of the theoretical.

In another experiment, the operation was carried out as described above, except that the heptylic acid (6 grams) was heated almost to boiling, then 3·5 grams of phosphoric anhydride added in small portions at a time, and the mixture heated again for about three minutes; the whole process required about six minutes. The ketone obtained, isolated as described above, weighed 0·95 gram, and 1 gram of unchanged acid was obtained from the alkaline residues. The yield in this experiment was, therefore, 25 per cent. of the theoretical.

The crude ketone can be easily obtained in a perfectly pure condition by dissolving it in methyl alcohol and reprecipitating with cold water; it separates from the solution in transparent, waxy plates melting at 30·5°.

An analysis of a portion which had been dried on a porous plate and then kept over sulphuric acid for 24 hours gave the following result:—

0·1608 gram of substance gave 0·4637 gram of CO_2 and 0·1886 gram of H_2O.

	Calculated for $C_{13}H_{26}O$.	Found.
C........	78·78 per cent.	78·65 per cent.
H........	13·13 ,,	13·03 ,,
O........	8·09 ,,	8·32 ,,

Dihexyl ketone (œnanthone) has been previously prepared by Uslar and Seekamp (*Annalen*, **108**, 179) by the distillation of calcium œnanthylate. In their paper, the authors state that various oily products are also formed in the reaction, and that the dihexyl ketone can be obtained in a pure condition (melting at 30°) only by repeated fractional distillation; the yield of ketone is not given, and its preparation in this way is evidently a tedious operation. Dihexyl ketone (melting at 30·5°) was also obtained in small quantities by Fittig (*Annalen*, **117**, 80) in a somewhat similar manner, together with large quantities of other products; the yield is not given, and the properties of the ketone are not described.

The dihexyl ketone obtained by the action of phosphoric anhydride on heptylic acid, after being once crystallised from dilute alcohol, melted at 30·5°, in agreement with Uslar and Seekamp's and Fittig's observations. It is very readily soluble in alcohol, ether, chloroform, light petroleum, and all organic solvents, but seemingly insoluble in water. If the aqueous distillate, referred to above, from which the ketone has been separated by filtration, is extracted with ether, and the dried ethereal solution evaporated, there remains only a trace of a yellowish oil which does not solidify on cooling. Dihexyl ketone is not very readily volatile with steam, but it distils without decomposition under the ordinary pressure. It seems to be only slowly oxidised by nitric acid or by an alkaline solution of potassium permanganate. That the compound obtained from heptylic acid, as described above, is in reality dihexyl ketone is proved, not only by its melting point and the results of analysis, but also by the formation of the oxime and the hydrazone, and by its behaviour on reduction.

Considerable quantities of bye-products are formed in the preparation of dihexyl ketone, and, after distilling the ketone (or acid) with steam, there remains in the flask a thick, almost black oil which can be easily isolated by extracting with ether. This substance has as yet only been superficially examined; it distils at a high temperature under greatly reduced pressure, yielding a thick, yellow liquid which has an odour recalling that of heptylic acid.

Oxime of Dihexyl Ketone, $(C_6H_{13})_2C{:}N{\cdot}OH$.

Dihexyl ketone oxime can be easily prepared by treating the ketone with hydroxylamine by Auwers' method. 1 gram of the pure ketone is dissolved in methyl alcohol, a dilute alcoholic solution of hydroxylamine hydrochloride (0·6 gram) and potash (2 grams) added, and the mixture heated to about 60°. After keeping for about 24 hours at the ordinary temperature, the alcohol is evaporated on the water-bath, the residue mixed with water and the solution acidified with dilute hydrochloric acid. The precipitated oil is then extracted with ether, the ethereal solution dried over calcium chloride and evaporated. The yellow oil obtained in this way was kept over sulphuric acid under reduced pressure for some days, and then analysed.

The following is the result:—

0·2005 gram of substance gave 12·3 c.c. of nitrogen, measured at 740 mm. and 16°.

	Calculated for $C_{13}H_{27}NO$.	Found.
N..........	6·6 per cent.	6·95 per cent.

Dihexyl ketone oxime is a yellowish oil which shows no signs of crystallising even when cooled below 0°; it is very sparingly soluble both in acids and alkalis, and seemingly insoluble in water, but miscible with alcohol, ether, &c., in all proportions.

Hydrazone of Dihexyl Ketone $(C_6H_{13})_2C{:}N{\cdot}NHPh$.

This compound was obtained by heating the pure ketone at 100° for about two hours with excess of phenylhydrazine and a little alcohol. The solution was then treated with water, the separated oil extracted with ether, and the ethereal solution washed well, first with dilute hydrochloric acid and then with water. On evaporating the dried ethereal solution, the hydrazone remains as a thick, reddish-yellow oil; it was kept for 48 hours over sulphuric acid under reduced pressure, and then analysed with the following result:—

0·2287 gram of substance gave 20 c.c. of nitrogen, measured at 740 mm. and 12°.

	Calculated for $C_{19}H_{32}N_2$.	Found.
N..........	10·0 per cent.	10·1 per cent.

Dihexyl ketone hydrazone is a moderately thick, reddish-yellow oil: it is insoluble in water and potash, but readily soluble in alcohol, ether, and other organic solvents. It dissolves sparingly in concentrated hydrochloric acid yielding a pink solution, but on keeping for a short time or heating gently, the hydrazone decomposes with evolution of gas. When heated in small quantities under the ordinary pressure, it decomposes with slight explosion, but without noise.

Dihexyl Carbinol, $(C_6H_{13})_2CH{\cdot}OH$.

Dihexyl carbinol can be easily prepared by reducing the ketone in the following manner:—The pure compound is dissolved in a considerable quantity of pure ether and the ethereal solution placed in a large flask or bottle provided with a reflux condenser and containing 100—200 c.c. of moderately concentrated caustic soda; sodium is then added, in small portions at a time, the total quantity employed being greatly in excess of that theoretically required for complete reduction. During the process, the ethereal solution gradually becomes turbid, owing to the separation of a colourless solid compound—probably the sodium-derivative of the alcohol—but on agitating with the aqueous solution, this substance disappears and the solution becomes clear again. The ethereal solution is then separated, the residual alkali extracted twice with ether, the combined ethereal solutions dried over potassium carbonate, and the ether evaporated.

Dihexyl carbinol is thus obtained in the form of a thick, yellowish oil which soon solidifies completely to a mass of crystals. It is best obtained in a pure condition by dissolving it in cold methyl alcohol and reprecipitating with water; if the addition of water causes the separation of an oil, it is advisable to cool the alcoholic solution in a freezing mixture before diluting, otherwise crystallisation takes place only after long standing. The colourless crystals are then separated by filtration and dried first on a porous plate and then over sulphuric acid.

An analysis of the crystalline alcohol gave the following result:—

0·1517 gram of substance gave 0·4324 gram of CO_2 and 0·1924 gram of H_2O.

	Calculated for $C_{13}H_{28}O$.	Found.
C........	78·0 per cent.	77·74 per cent.
H........	14·0 „	14·09 „
O........	8·0 „	8·17 „

Dihexyl carbinol separates from dilute alcohol in colourless, transparent plates melting at 41—42°; it has a peculiar sweet odour, and is very readily soluble in light petroleum, benzene, chloroform, alcohol, and other organic solvents, but insoluble in water. When heated in small quantities under the ordinary pressure, it distils without decomposition, and the distillate quickly solidifies on cooling. When treated with cold concentrated hydrobromic acid, the crystals melt to a yellowish oil, but do not dissolve in the acid; on diluting with water, this oil solidifies to colourless plates which melt at 38—39°. This compound is doubtless the bromide, $(C_6H_{13})_2CHBr$, as it contains considerable quantities of bromine.

Preparation of Stearone $(C_{17}H_{35})_2CO$.

The stearic acid employed in these experiments was obtained by repeatedly recrystallising the crude commercial acid from strong alcohol; that the acid was pure is shown by its melting point (68—69°) and by the following analysis:—

0·1490 gram of substance gave 0·4150 gram of CO_2 and 0·1692 gram of H_2O.

	Calculated for $C_{18}H_{36}O_2$.	Found.
C........	76·05 per cent.	75·96 per cent.
H........	12·67 „	12·61 „
O........	11·28 „	11·43 „

It is perhaps a fact worthy of remark that stearic acid which has been crystallised from alcohol retains some of the solvent even after long exposure to the air on a porous plate, and its melting point is thereby lowered considerably.

For the preparation of stearone, the following method was employed:—9·5 grams of pure stearic acid are placed in a small beaker and heated at 210° in a metal- or oil-bath; 5 grams of phosphoric anhydride are then added in small portions at a time, the mixture being stirred well during the process. At first, considerable effervescence takes place, owing to the liberation of carbonic anhydride, as can be easily proved in the usual manner; towards the end of the operation, no further evolution of gas occurs. The dark-brown mass is allowed to cool, and then gradually stirred up with water. A considerable quantity of phosphoric anhydride remains unchanged, as is shown by the development of heat on adding water, and it is probable that a better yield of ketone would be obtained by using less anhydride than the quantity given above; if, on the other hand, too small a quantity of phosphoric anhydride were employed, some of the stearic acid would remain unchanged and the purification of the ketone would be less simple. After adding excess of soda or potash, the mixture is warmed gently, with frequent stirring, for about 15 minutes, then allowed to cool, diluted with water, and the alkaline solution of phosphate separated by filtration, or more quickly, by decantation; it has been found advisable not to boil the alkaline liquid, as, if this be done, a sort of emulsion is formed and the insoluble products cannot easily be separated.

The insoluble wax-like mass is washed with water, transferred to a flask, and repeatedly extracted with strong alcohol. This process is greatly facilitated if some filter-paper is placed in the flask; the insoluble oily products are then absorbed by the paper, and the alcoholic extract remains quite clear, so that it is unnecessary to filter the solution. On cooling, the alcoholic extracts deposit the stearone completely in the form of a yellowish powder; it is separated by filtration and dried on a porous plate.

The yield of crude stearone was 3·5 grams from 9·5 grams of stearic acid, or 41 per cent. of the theoretical quantity. Only two experiments with stearic acid have as yet been made, so that it is probable that the process can be considerably improved.

The crude product is almost pure, and melts at about 84—85°; by crystallising it twice or three times from alcohol, it is obtained in a perfectly pure condition, and then melts at 88°.

Analyses of two different samples of the pure compound, dried at 100°, gave the following results:—

I. 0·1323 gram of substance gave 0·4026 gram of CO_2 and 0·1643 gram of H_2O.

II. 0·1420 gram of substance gave 0·4316 gram of CO_2 and 0·1771 gram of H_2O.

	Calculated for $C_{35}H_{70}O$.	Found.	
		I.	II.
C	83·00 p. c.	82·99	82·88 p. c.
H........	13·83 „	13·83	13·85 „
O........	3·17 „	3·18	3·27 „

Stearone has been previously prepared by Heintz (*Jahresb.*, 1855, 515—516) by the distillation of stearic acid alone or with lime; also by Krafft (*Ber.*, **15**, 1715), by the distillation of calcium stearate under reduced pressure. I have not been able to refer to Heintz's paper, but Krafft, who improved the original process, states that the yield does not amount to half the theoretical.

By the method described above, stearone can be easily obtained in a pure condition in the course of a few hours with comparatively little trouble, and the yield, as already mentioned, is at least 40 per cent. of the theoretical. It is necessary, however, that the pure acid should be employed; in some experiments with a sample of the commercial acid, melting at about 62°, the ketone obtained melted at 75—76°, even after being repeatedly recrystallised from alcohol, probably owing to the presence of palmitone and other homologues.

It is stated in "Beilstein" (1886, p. 421) that when stearic acid is heated with phosphoric anhydride, it yields a compound of the composition $C_{18}H_{34}O$ which melts at 54—60°, and is insoluble in alkalis. I have not been able to detect the formation of any substance of this nature; it is evidently not present as impurity in the stearone, because, if it were, the analyses would indicate the fact, the two compounds $C_{35}H_{70}O$ and $C_{18}H_{34}O$ differing considerably in composition, especially as regards the percentage of hydrogen which they contain. As is the case with heptylic acid, a considerable quantity of bye-products are formed in the action of phosphoric anhydride on stearic acid; after extracting the product with alcohol until ketone ceases to be deposited on cooling, there remains a brown, waxy substance which is practically insoluble in alcohol, but readily soluble in benzene or light petroleum. This product has not yet been examined, but it seems hardly probable that it should be a compound of the composition $C_{18}H_{34}O$.

Stearone Oxime, $(C_{17}H_{35})_2C{:}N{\cdot}OH$.

For the preparation of this compound 0·7 gram of the stearone, obtained as described above, was dissolved in hot alcohol, 0·3 gram of hydroxylamine hydrochloride and 0·5 gram of potash, dissolved in a little dilute alcohol, added to the solution, and the mixture boiled in a flask, provided with a reflux condenser, for about two hours. The solution, on cooling, deposited a colourless powder which was separated by filtration, washed well with very dilute hydrochloric acid, then with water, and dried on a porous plate.

This substance is stearone oxime, as is shown by the following analysis:—

0·2514 gram of substance gave 6·6 c.c. of nitrogen, measured at 755 mm. and 14°.

	Calculated for $C_{35}H_{71}NO$.	Found.
N..........	2·68 per cent.	3·07 per cent.

It separates from hot alcohol as a colourless, seemingly amorphous powder and melts at 63°; it is moderately easily soluble in boiling benzene and hot alcohol, but insoluble in alkalis, acids, and water.

Heriot Watt College,
Edinburgh.

XXXIII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. XVIII. *On the Sulphates of Antimony.*

By R. H. ADIE, B.A., Scholar of Trinity College.

1. THE compounds of antimonious oxide and sulphuric acid do not appear to have received a very complete investigation, judging by the published results. Hence I decided to examine these compounds, as I had previously done in the case of arsenious oxide and sulphuric acid (Trans., **55**, 1889, 157).

2. In 1871, Schultz-Sellach (*Ber.*, **4**, 109) described the preparation of the compound $Sb_2O_3,4SO_3$ from antimonious oxide and fuming sulphuric acid; his analysis gave Sb_2O_3, 47·44 per cent., and SO_3, 53·08 per cent. In a previous paper (*Ber.*, **4**, 13), he described the preparation of the normal sulphate $Sb_2(SO_4)_3$ by dissolving Sb_2O_3 in tolerably concentrated sulphuric acid. Basic sulphates have also been described, to which simple formulæ have been assigned, as $Sb_4O_5(SO_4)$, by Péligot.

3. As in the case of arsenious oxide, I started with fuming acid, then tried concentrated acid and sulphuric anhydride, and, finally, dilute acids and the action of solvents.

4. *Sulphuric Anhydride.*—Sb_2O_3 when dropped into liquid SO_3, formed hard flakes, insoluble in excess of SO_3, even when heated in a sealed tube at 180°. The flakes agglomerated on heating, and then the cake formed was freed from adhering SO_3 by tilting the tube and keeping the end containing the compound warm until the SO_3 solidified.

Specimens prepared as above by heating to different temperatures gave on analysis :—

	I. 120°.	II. 120°.	III. 160°.	IV. 180°.
SO_3	55·87	61·55	73·55	74·56

Calculated for		
$Sb_2O_3,8SO_3$.	$Sb_2O_3,9SO_3$.	$Sb_2O_3,10SO_3$.
68·98	71·45	73·52

The results show that the formation of the compound of Sb_2O_3 with the highest proportion of SO_3 requires a temperature of about 160°. The compound formed at that temperature would seem to have the formula $Sb_2O_3,9SO_3$, but as the corresponding arsenic compound can be freed completely from excess of SO_3, and is probably $As_2O_3,8SO_3$, it would perhaps be best to assume that the antimony compound possesses the same formula, viz., $Sb_2O_3,8SO_3$. Considering the difference of density of Sb_2O_3 and of SO_3, the adhering sulphuric anhydride would probably not exceed 2—3 per cent.

It is decomposed by water with formation of a basic salt.

5. *Fuming Sulphuric Acid.*—The acid used, as in the case of arsenic, contained about 88 per cent. of SO_3, and was approximately $2H_2SO_4,SO_3$.

The oxide formed, as in § 4, a hard cake which is not readily soluble. Its solubility, though not so great as the corresponding arsenic sulphate, increased largely with rise in temperature. The product crystallised in fine needles, which, on recrystallisation, were practically pure $Sb_2O_3,4SO_3$.

	1st crystallisation.	2nd crystallisation.	Calculated for $Sb_2O_3,4SO_3$.
SO_3......	50·93	53·70	52·63

The mother liquor only contained a small quantity of the sulphate. $Sb_2O_3,4SO_3$ decomposes on exposure to the air and by the action of water.

6. *Concentrated Sulphuric Acid containing* 98 *per cent.* H_2SO_4.—Sb_2O_3 is very soluble in boiling sulphuric acid. On cooling, a large quantity of crystals separate out, which, on recrystallisation, are pure $Sb_2(SO_4)_3$.

	1st crystallisation.	2nd crystallisation.	Calculated for $Sb_2(SO_4)_3$.
SO_3......	43·91	46·98	45·45

$Sb_2(SO_4)_3$ decomposes quickly on exposure to the air. The results of its decomposition by water, &c., are detailed in § 8.

7. *Dilute Sulphuric Acids.*—(i.) I have found the strength of acid limiting the formation and existence of $Sb_2(SO_4)_3$ in solution.

From $9H_2SO_4,6H_2O$ the product contained 47·40 p. c. SO_3.
„ H_2SO_4,H_2O „ „ 50·65 „

These results show that the normal or trisulphate is formed from sulphuric acid of concentrations between the limits H_2SO_4 and H_2SO_4,H_2O inclusive.

(ii.) From $H_2SO_4,2H_2O$ a new compound was obtained, namely, the basic sulphate $Sb_2O_3,2SO_3,H_2O$ or $Sb(OH)SO_4$. It may be crystallised by slow cooling, and gave the following results:—

	I.	II.	III.	IV.	Calculated for $Sb_2O_3,2SO_3,H_2O$.
Sb_2O_3..	—	—	—	62·16	61·7
SO_3...	35·75	35·54	34·64	—	34·3
H_2O...	—	—	—	3·99	4·0

This sulphate gives off its water at 100°, but suffers no further decomposition until above 250°.

(iii.) From $H_2SO_4,4H_2O$, the compound separates out in small quantity as a fine powder, which it is difficult to free from adhering acid. At last I obtained one crystalline preparation by allowing the sulphate to remain in the mother liquor for about a month at 20°, (about) and the crystals thus obtained determined the deposition from the cooling solution of a crystalline sulphate, $Sb_2O_3,2SO_3,3H_2O$, or $Sb(OH)SO_4,H_2O$.

Analyses:—

					Calculated for.	
	I.	II.	III.	IV.	$Sb_2O_3,2SO_3,3Aq$.	$Sb_2O_3,2SO_3,4Aq$.
Sb_2O_3..	—	54·15	55·35	—	57·37	55·39
SO_3...	31·88	30·68	—	—	31·87	30·69
H_2O...	—	—	11·19	10·24	10·76	13·93

The crystals are scarcely decomposed by cold water, slowly by boiling water, and are not rapidly dissolved by boiling dilute hydrochloric acid. They are decomposed at 100°, at which temperature they lose all their water. The justification of the arrangement of my formula is found in the existence of the compound $Sb(OH)SO_4$ in (ii).

Antimonious oxide is so little soluble in acids more dilute than $H_2SO_4,4H_2O$ that I next proceeded to the investigation of—

8. *The Action of Solvents on Antimony Sulphate.*—Péligot states that by the decomposition of $Sb_2O_3,4SO_3$ by cold water the basic salt $Sb_4O_5(SO_4)$ is formed. I repeated this to see whether he might have passed over any loosely combined water, using the trisulphate instead of the tetrasulphate.

Dry $Sb_2(SO_4)_3$ was decomposed and washed till the washings were free from sulphuric acid.

(i.) *By Water at* 100°.—The compound, that is, the basic sulphate obtained by this method, is approximately $7Sb_2O_3,2SO_3,3Aq$; this represents the limit of the decomposition of the sulphate by water.

Results of analysis:—

	I.	II.	III.	Calculated for $7Sb_2O_3,2SO_3,3Aq$.
SO_3	7·03	6·50	—	7·05
H_2O....	5·16	4·57	33·59	4·73

I and II were dried by standing on a porous plate in air, I for five weeks, II for three days; III was pressed between porous plates till dry (see § 9).

(ii.) *By Cold Water.*—The basic salt, dried at 100°, is $2Sb_2O_3,SO_3$, as found by Péligot.

	I.	II.	III.	IV.	V.	VI.	Calculated for $2Sb_2O_3,SO_3$.
SO_3..	11·62	11·47	13·23	10·18	11·30	11·58	12·19

I to IV were decomposed by water at about 18°, V and VI by water at about 6°.

The water was estimated separately in preparations dried in various ways. In the following table the second column contains the results for the sulphate decomposed at 18°, and the third for that at 6°. In each case I, II, and II were allowed to stand in air on a porous plate in a fine state of division, I (at 18° only) for five weeks, and II and III for about three days; IV was dried by pressure between dry porous plates, and V by pressure between filter-papers.

Percentages of water only:—

	18°.	6°.	Calculated for.	
I	10·76	4·75	$2Sb_2O_3,SO_3,2Aq$	5·20
II	7·31	5·58	„ 3Aq	7·30
III	10·48	7·21	„ 4Aq	9·88
IV	27·85	32·37	„ 5Aq	12·05
V	38·55	—	„ 10Aq	21·50
			„ 16Aq	30·51

(iii.) *By Absolute Alcohol* (18°).—The basic salt, when dried at 100°, only lost 2·2 per cent., and is $Sb_2O_3,2SO_3$.

Analysis gave—

		Calculated for $Sb_2O_3,2SO_3$.
SO_3............	35·11	35·71

9. From these tables it is seen that the removal of the SO_3-groups from the sulphate by means of water is accompanied by the substitution of a considerable amount of water therefor. When the product is dried rapidly by pressure between porous plates, the quantity of water retained, in all cases, is about 30 per cent., which corresponds roughly to $2Sb_2O_3,SO_3,16Aq$. This substance is rather akin to the cryohydrates than to the ordinary hydrates, since it parts with its attached water to the air at about 15—18°; even after prolonged drying in air, the product of the action of cold water retains about 10 per cent. of water, and is thus approximately $2Sb_2O_3,SO_3,4Aq.$, while that of the action of ice-cold and hot water respectively only retains about 5 per cent. of water in each case, and is thus approximately $2Sb_2O_3,SO_3,2Aq$.

We seem to have here some evidence for the existence of complex hydrates, such as may be supposed to exist in solution.

10. I have here arranged the complete series of antimony sulphates now described in a column parallel with the arsenic sulphates prepared from the same acids.

SO_3.	$As_2O_3,8SO_3$.	$Sb_2O_3.8SO_3$.
$2H_2SO_4,SO_3$.	$As_2O_3,4SO_3$	$Sb_2O_3,4SO_3$.
H_2SO_4. $9H_2SO_4,3H_2O$ to H_2SO_4,H_2O.	$As_2O_3,2SO_3$ As_2O_3,SO_3	$Sb_2O_3,3SO_3$, or $Sb_2(SO_4)_3$.
$H_2SO_4,2H_2O$.	—	$Sb_2O_3,2SO_3,H_2O$, or $Sb(OH)SO_4$.
$H_2SO_4,4H_2O$.	—	$Sb_2O_3,2SO_3,3H_2O$, or $Sb(OH)SO_4,H_2O$.
Action on sulphate of—		
Alcohol.	—	$Sb_2O_3,2SO_3$, or $SbO(SO_4)_2$.
Cold water.	As_2O_3.	$2Sb_2O_3,SO_3,xAq$.
Hot water.	—	$7Sb_2O_3,2SO_3,yAq$.

Where $x = 4$ to 16 and $y = 2$ to 16.

On comparing the two series of compounds, it appears that:—

(i.) With H_2SO_4 and weaker acids, Sb_2O_3 forms a different order of sulphates from As_2O_3, while it resembles it in forming acid sulphates when subjected to the action of stronger acids. The characteristic group salt $Sb_2(SO_4)_3$, which is formed by the former, is replaced by the basic $As_2O(SO_4)_2$ in the latter case. The limits of existence, both as regards dilution and temperature, are much narrower for the arsenic than for the antimony salt. The practically complete formation of $Sb_2(SO_4)_3$ in one crystallisation also contrasts with the formation of $As_2O(SO_4)_2$ only by repeated crystallisation.

(ii.) Arsenious oxide does not form any basic sulphates containing water, whilst the oxide of the more metallic antimony does form hydrated sulphates in acids weaker than H_2SO_4,H_2O. This acid is the limit of existence of $Sb_2(SO_4)_3$ in solution and of any arsenic sulphate whatever.

(iii.) In contrast to the case of the arsenic compounds, one cannot remove all the SO_3 from the antimony sulphates by water. The stability of the latter in dilute acids far exceeds that of the former.

In conclusion, I have great pleasure in thanking Mr. Pattison Muir for the use of his laboratory during this work, and for his kind attention and assistance during its progress.

I hope to be able to communicate the results of some work on the compounds of phosphorus and sulphur trioxide in a short time.

XXXIV.—*Phosphorous Oxide.* Part I.

By T. E. Thorpe, F.R.S., and A. E. Tutton, Demonstrator of Chemistry in the Normal School of Science, South Kensington.

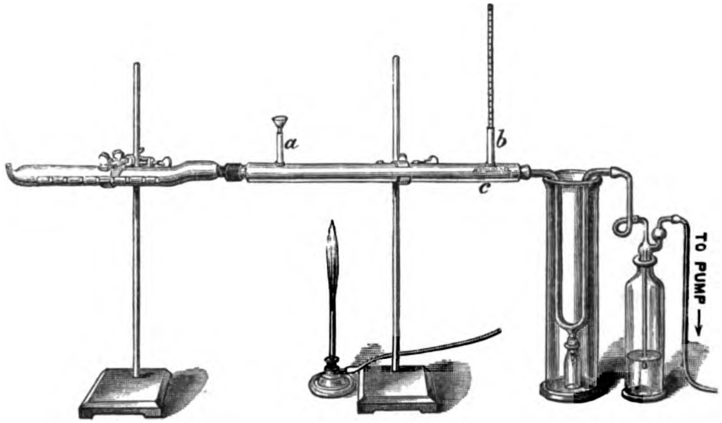
In the course of the preparation of *Phosphorus tetroxide*, P_2O_4, as described in the communication we brought before the Society in November, 1886 (Trans., 1886, 833), we frequently noticed the occurrence of a sublimate of long, radiating, feathery crystals, which were evidently very volatile, inasmuch as they could be readily vaporised in a current of nitrogen or carbon dioxide at a temperature below 100°, and which were also very fusible, since the mere warmth of the hand caused them to melt. After the completion of the work on the tetroxide we turned our attention to these crystals, and made a number of experiments in order to determine their nature and the conditions under which they were formed. Our method of making phosphorus tetroxide consisted in burning phosphorus in a slow current of dry air, collecting the products of combustion in a glass tube surrounded by an outer tube filled with steam, transferring the products to a tube closed at one end and previously filled with dry carbon dioxide. This was then exhausted by the Sprengel pump, sealed, and heated to 280—300°, when a sublimate of colourless, highly lustrous crystals of the tetroxide formed in the upper part of the tube. As the result of preliminary experiments on the conditions of formation of the readily volatile, fusible crystals, it was found that their yield was greatly augmented by increasing the rapidity of the air-current. When a few grams of phosphorus were burnt at one end of a long, horizontally-placed combustion-tube in a rapid stream of dried air, drawn through the apparatus by a water-pump, the greater part of the inner surface of the tube was found to be covered with the feathery crystals, which readily melted when the outside of the tube was touched with the finger. It was further noticed that the deposition of the crystals was increased by cooling the outside of the tube with iced water. If the combustion was allowed to proceed until all the phosphorus was burnt, the crystals were apt to take fire and to burn to white, amorphous flocks consisting, apparently, of the pentoxide. The white, volatile, crystalline substance was readily separated from the amorphous oxides simultaneously produced in the combustion-tube in the following manner:—As soon as a fairly large deposit of the crystals was formed upon the upper part of the tube, and when, at most, three-fourths of the phosphorus employed was burnt, the further end of the tube was adapted to a U-shaped condenser placed in a freezing mixture, a loose plug of glass wool being placed in the front portion of the condensing tube to arrest any finely-divided, amorphous oxide which might be carried over. The portion of the tube containing the crystals was then heated to about 100° by means of the steam-jacket previously referred to, in a slow stream of dry carbon dioxide. The volatile substance was then transferred to the condensing tube, an almost perfect separation from the amorphous oxides being effected. The product in the tube readily melted with the warmth of the hand. Water seemed to have very little action upon it. It could be melted by the heat of the hand under the water, but the two liquids did not mix. On long standing—two or three days in the case of half a gram of the substance—it slowly dissolved, and the solution gave all the reactions of *phosphorous acid.*

This behaviour is so entirely dissimilar from that usually attributed to phosphorous oxide that we determined to submit the volatile crystalline substance to a closer investigation. Steps were next taken to ascertain its composition. In the first place, it was proved to contain neither hydrogen nor nitrogen by burning dry phosphorus in a mixture of equal volumes of dry carbon dioxide and oxygen. Clean, nearly colourless phosphorus, dried by means of filter-paper, was melted under several successive portions of absolute alcohol and then washed with benzene previously carefully dehydrated by sodium. The benzene was finally removed *in situ* in the combustion-tube by the aid of a current of the mixture of carbon dioxide and oxygen dried by passing, first, through 6 feet of U-tubes containing pumice and sulphuric acid, and then through 12 feet of tubing filled with phosphorus pentoxide. As soon as the last traces of benzene had disappeared, the combustion was started by gently warming the phosphorus, when the usual yield of crystals was obtained. Hence the only possible elements present were phosphorus and oxygen. About 0·2 gram of the product, which melted to a clear, transparent liquid, was then cautiously oxidised by means of nitric acid. The reaction is so extremely violent that it is quite impracticable to conduct the operation in a sealed tube in the usual manner. The product was therefore placed, together with a few c.c. of water, in a small U-tube, one limb of which was drawn out and bent so as to dip into a small beaker containing strong nitric acid, the other limb being furnished with a small tap-funnel, also containing nitric acid. The oxidation proceeded with considerable violence, but with care all loss was avoided, the escaping fumes being absorbed by the nitric acid in the beaker. The substance contained 56·17 per cent. of phosphorus; P_2O_3 requires 56·36 per cent. of phosphorus. The inference was, therefore, that the crystalline, volatile substance actually was phosphorous oxide, but that the properties of this body are very different from those usually ascribed to it in the text-books.

The fact that when phosphorus burns in the air there is formed a white, solid substance condensing as a loose, light, flocculent powder, was noticed by Boyle, but the first special study of this compound was made in 1740 by Marggraf, who termed it *flowers of phosphorus.* The existence of phosphorous oxide seems to have been discovered by Sage, who, however, appears to have confounded it with the product obtained by Marggraf. Lavoisier ("Sur la Combustion du Phosphore de Kunckel": *Mém. de l'Académie des Sciences*, 1777, 65) surmised that the product varied with the conditions under which the phosphorus was burnt, and he inferred the existence of two oxides of phosphorus which he imagined stood in the same relation to phosphorus as the oxides of carbon did to carbon. The true phosphorous acid was first prepared by Davy, in 1812, by the action of water upon phosphorus trichloride: but the difference between this body and that obtained by the limited oxidation of phosphorus was first indicated by Dulong in 1816 (*Ann. Chim. Phys.*, 1816, **2**, 141).

Preparation of Phosphorous Oxide.—In our earlier trials the yield of phosphorous oxide was very small; but during the course of the investigation various improvements have been effected in the mode of preparation, with the result that about 30 grams of the nearly pure substance may now be obtained in an experiment of six hours' duration, and, by systematic work, as much as a couple of hundred grams have been accumulated in a few days' time. The arrangement of the apparatus we now employ is seen in Fig. 1. The dried phosphorus, of which about two sticks are used in each preparation, is placed in pieces about an inch long in a combustion-tube of about $1\frac{1}{2}$-inch bore, bent into the shape shown in the figure so as to prevent the melted phosphorus from escaping. The combustion-tube is open at one end to admit the air, which need not be dried, and at the other is fitted into a brass tube surrounded by a wider brass tube. The space between the metal tubes is filled with water introduced by means of the vertical supply tube (*a*); the second tube (*b*) screwed into the outer brass jacket contains a thermometer to indicate the temperature of the water. Into the further end of the inner brass tube is pushed a loose plug of glass wool (*c*) about 2 inches long, and the U-shaped condenser is then fixed to the tube by means of an ordinary cork. At the bottom of the bend of the U-tube is fixed a short, vertical stem which is connected by means of a well-fitting stopper with a little bottle to which the oxide can be transferred by melting it away from time to time from the sides of the condensing tube. The U-tube is connected with a jet-pump, by the aid of which the air is drawn over the burning phosphorus, and between the pump and the condenser is placed a bottle containing oil of vitriol; this prevents the diffusion of water-vapour into the apparatus, and serves also to indicate the speed of the air-current. The U-tube and bottle are surrounded by a freezing mixture of ice and salt; the U-tube should have limbs at least a foot long, and should not be too wide, otherwise considerable loss may occur through imperfect condensation. Indeed, it is of advantage to employ two such condensers, placed one after the other, as with a high speed of air a notable amount of the oxide is thus

FIG. 1.



prevented from escaping. When everything is ready, the jet-pump is set in action, and the temperature of the phosphorus is raised to the ignition point by a small flame held for a moment near the anterior end of the combustion-tube. As regards the speed of the air-current, it has been found that the yield of the oxide increases with the quantity of air drawn over the burning phosphorus in a given time. This, at first sight, seems opposed to the view that the phosphorous oxide is only formed in a slow current of air; as a matter of fact, the most rapid combustion that is practically possible under the circumstances is but a slow and, relatively, feeble burning when compared with that which occurs in the open air. If the combustion is too local, it may happen that the main product of the action is phosphoric oxide. In a well-conducted experiment, large quantities of the red oxide, P_4O, are always formed in the portion of the tube nearest the burning phosphorus. When the phosphorus has been burning in the rapid current of air for about a quarter of an hour, the outer brass tube and the water are heated until the thermometer indicates about 50°. This temperature is maintained until near the end of the experiment, when it may advantageously be raised to 60°. In about half an hour after the ignition of the phosphorus, the oxide begins to make its appearance in the condenser. If the glass wool is properly packed (the plug should not be too tight), not a trace of the pentoxide will pass over into the condenser; and if the temperature of the water-jacket is not allowed to exceed 60°, only very small quantities of free phosphorus find their way into the U-tube. Most of that which passes over is found in small globules in the upper part of the condenser and close to the heated jacket. As the readily-fusible oxide collects and runs over into the cooled U-tube, it solidifies to a snow-white, wax-like mass. The experiment should be terminated when about four-fifths of the phosphorus has been burnt, in order to avoid the oxidation of the product. The condensing U-tube is detached and the oxide melted down into the small bottle, from which it is transferred to the store-bottle previously filled with dry carbon dioxide. This should be fitted with a carefully-ground stopper, and it should be kept in the dark in an atmosphere of carbon dioxide, dried by means of phosphoric oxide.

Analysis of Phosphorous Oxide.—That the product thus obtained is practically pure phosphorous oxide is shown by the following analyses made with different preparations:—

I. 0·2170 gram gave 0·2792 gram P_2O_5, or 56·17 per cent. phosphorus.

II. 0·5966 gram gave 1·2051 grams $Mg_2P_2O_7$, or 56·41 per cent. phosphorus.

III. 0·8515 gram gave 1·7330 grams $Mg_2P_2O_7$, or 56·84 per cent. phosphorus.

The percentage of phosphorus corresponding to P_2O_3 = 56·36.

Analysis I was made by the lime method, described by the authors in the paper on phosphorus tetroxide (Trans., 1886, 836). In the others, the oxide, contained in a small tube, was covered with water and cautiously treated with bromine. The oxide was then slowly dissolved, and converted into phosphoric acid. In order to make sure that the acid was transformed into the ortho-variety, the solution was evaporated several times with nitric acid, and the phosphoric acid was then precipitated with magnesia-mixture, and treated in the usual way.

Phosphorous oxide melts at 22·5° to a clear, colourless, and very mobile liquid, which resolidifies at 21°. It has a marked tendency to remain liquid at temperatures several degrees below its ordinary solidifying point, especially when enclosed in narrow tubes such as are generally employed in making determinations of melting point. Thus in one experiment a quantity of the liquid was cooled down to 16·5° without solidifying. Just below this temperature it suddenly and completely solidified. When only a portion of the substance is liquefied, it resolidifies sharply at 21°, on allowing the temperature to fall to this point. A quantity of the fluid substance, which remains liquid at 21°, may be immediately solidified by introducing a small portion of the solid. In this respect the oxide resembles phosphorus, which exhibits the property of superfusion in a high degree.

Phosphorous oxide boils constantly and without decomposition at 173·1° (corrected), when heated in an atmosphere incapable of acting upon it, such as nitrogen or carbon dioxide. In the course of the work the following determinations of boiling points have been made upon different preparations:—

Weight of oxide distilled.	Corr. b. p.	Weight of oxide distilled.	Corr. b. p.
6 grams	173·0°	50 grams	173·0°
6 ,,	173·3*	8 ,,	173·0
32 ,,	173·4*	7 ,,	173·0
20 ,,	173·1	45 ,,	173·3*

Mean .... 173·1°.

In the case of the determinations marked with an asterisk, the whole of the mercury column was heated by the vapour. In the others a correction was applied for the emergent column by the formula given by one of us in the paper on Specific Volumes (Trans., 1880, 159). All the values are reduced to the standard pressure of 760 mm.

Determination of Molecular Weight of Phosphorous Oxide.—The density of the oxide in the gaseous state was determined by Hofmann's method in the Torricellian vacuum. At the temperature of boiling amyl alcohol, 132°, the vaporisation is complete, and two determinations were made at this point; two at the temperature of boiling oil of turpentine, 159°; and two at that of boiling aniline, 184°. At these temperatures, even in contact with the heated mercury, the substance is practically unaltered, a minute trace of a red deposit, due possibly to a slight admixture of free phosphorus, or caused by the action of light upon the substance (*v. infra*), being left in the bottle in which the oxide had been passed up into the tube. This trace of solid residue would cause a slight diminution in the apparent volume of gas, and hence a slight increase in the value obtained for the vapour-density. The results are as follows:—

Weight of substance in grams.	Temp. (T).	Bar. mm.	Pressure on gas. mm.	Vol. of gas at T° (c.c.).	Density. Air = 1.
0·1887	132·0°	770·0	156·0	137·5	7·67
0·1887	131·0	769·0	154·0	137·5	7·75
0·1887	159·0	769·0	162·8	139·6	7·71
0·1887	184·0	769·0	170·0	141·4	7·69
0·3213	158·0	776·0	249·1	153·3	7·81
0·3213	183·5	777·5	259·0	155·6	7·83

The density corresponding to the formula P_2O_3 is 3·81; that corresponding to P_4O_6 is 7·62. *Hence the molecule of phosphorous oxide in the gaseous state is represented by the formula* P_4O_6. In this respect it is analogous to arsenious and antimonious oxides, which have been shown by Victor Meyer to have the molecular formulæ As_4O_6 and Sb_4O_6 respectively (*Berichte*, **12**, 1117 and 1284).

An attempt was next made to determine if a higher temperature would effect the dissociation of the P_4O_6 molecule; it was found, however, that at about 300° the substance was completely decomposed. The nature of the decomposition will be described hereafter (*v.* p. 552).

Determination of Molecular Weight of Phosphorous Oxide by Raoult's Method.—As benzene was found to dissolve phosphorous oxide without change, a determination of the molecular weight of the substance could be made by Raoult's method, using benzene as a solvent. 0·6760 gram of the oxide was dissolved in 20·698 grams of benzene, thus forming a 3·16 per cent. solution. The reading of the freezing point of the pure benzene was 3·45°; for the 3·16 per cent. solution it was 2·77°. A depression of 0·68° was thus observed. As 49 is

Raoult's constant for benzene, the molecular weight is, therefore, $\frac{3{\cdot}16 \times 49}{0{\cdot}68} = 227$. The molecular weight corresponding to P_4O_6 is 220. Hence this result confirms that obtained by the determinations of the vapour-density, and shows that phosphorous oxide is represented by the formula P_4O_6.

Action of Heat.—Phosphorous oxide is a comparatively stable substance up to temperatures of about 200°. When heated in a sealed tube, the clear liquid becomes turbid at about 210°, and at a somewhat higher temperature the solid substance which separates out gradually becomes yellow, and ultimately dark-red. At 300°, a considerable quantity of the red solid is formed, but there is still a large proportion of the liquid undecomposed, even after an hour's heating at this temperature. At the temperature of boiling sulphur, 440°, the whole of the oxide is decomposed into solid products. A sublimate of ordinary phosphorus is found at the top of the tube, together with a less volatile deposit, which lines the interior of the tube just beyond the portion immersed in the sulphur vapour, and consists of colourless, highly-refracting crystals, identical in their crystallographical characters and chemical properties with the phosphorus tetroxide described by us on a former occasion (Trans., 1886, 833). The decomposition of phosphorous oxide by heat may, therefore, be represented by the equation $2P_4O_6 = 3P_2O_4 + P_2$.

As this decomposition of phosphorous oxide affords a ready mode of preparing phosphorus tetroxide, we propose to resume our study of the latter compound, and attempt to complete its physical and chemical history.

Action of Light on Phosphorous Oxide.—It is well known that samples of commercial phosphorus pentoxide occasionally turn more or less yellow on exposure to strong light. Such samples have invariably the characteristic garlic smell usually attributed to phosphorus, and hence the change of colour has been ascribed to the presence of small quantities of that element in the product. The light, flocculent powder, obtained by the slow burning of phosphorus in a limited supply of air, consists of phosphoric pentoxide, phosphorous oxide, and free phosphorus. This product, which is apt to ignite in contact with the air, rapidly turns yellow, and ultimately red, on exposure to sunshine, the change being also attributed to the action of light upon the finely-divided phosphorus. In Regnault-Strecker's *Lehrbuch der Anorganischen Chemie*, p. 417, ed. 1877, the alteration in colour is assumed to be due to the action of light upon the phosphorous oxide, which is supposed to be decomposed in accordance with the equation $5P_2O_3 = 4P + 3P_2O_5$.

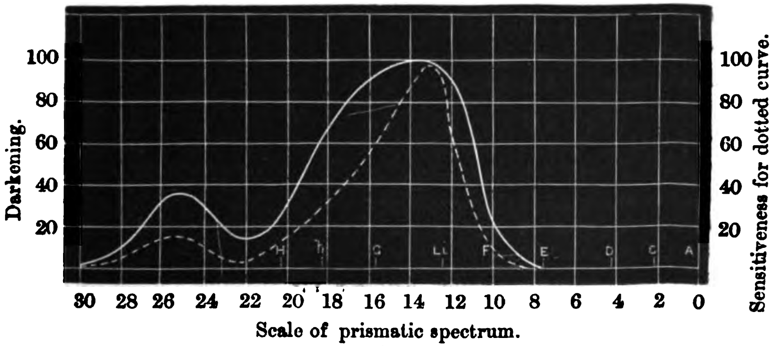
The Rev. Dr. Irving, in a paper read at the meeting of the British

Association in 1883 (*Chem. News*, **48**, 173), drew attention to this action, which Professor Liveing suggested might be due to the heat into which the luminous solar radiation was transformed by absorption. Cowper and Lewes (Trans., 1884, 10) examined the deposit thus obtained, and came to the conclusion that it was a mixture containing minute crystals of phosphorus, in quantity varying from 17 to 27 per cent., which were changed to the red modification when exposed to sunlight, and that the spontaneous inflammability claimed for phosphorous anhydride was probably due to the same cause.

There is no question, however, that phosphorous oxide is rapidly acted upon by light. Even diffused daylight slowly turns it yellow, and in strong sunshine the change is very rapid. Portions of the pure oxide, contained in sealed tubes previously filled with carbon dioxide, became orange-yellow, and ultimately dark-red, on exposure for an hour or two to the comparatively feeble sunshine of winter. In one experiment, a quantity of pure phosphorous oxide, which had been exposed for 11 weeks to such sunshine as a London winter affords, became of the dark-red colour of amorphous phosphorus. The undecomposed oxide was melted by heating to 25—30°, decanted from the red precipitate, and re-distilled; it was perfectly clear and colourless, and solidified to a pure white mass of crystals. On again exposing it to sunshine, it became yellow within about 10 minutes, and eventually red as before.

Captain Abney has kindly made some observations for us on the effect of sunlight on the oxide, and has furnished us with the annexed diagram (Fig. 2), which serves to indicate the particular light vibrations which are mainly concerned in determining the change.

Fig. 2.—Action of Light on Phosphorous Oxide.



A small, thin glass tube containing the substance was placed in a solar spectrum, measuring $1\frac{1}{2}$ inches in length from A to H. The slit was fairly wide, about $\frac{1}{50}$ inch, and the exposure lasted three hours. The scale of the spectrum being known, the relative positions of the different portions of the oxide in the horizontally placed tube with respect to the spectrum were also known.

The amount of change effected was measured by comparing the intensity of the orange colour produced with grey tints, according to the method employed by Captain Abney in his colour photometry, and the results are plotted out as shown. The curve cannot be taken as anything more than a fair approximation to the amount of the change produced. It is not a measure of the actual sensitiveness of the compound to the different parts of the spectrum. The sensitiveness is in reality much higher at 13 of the scale than at 16 or 12, for instance, or, in other words, the curve of sensitiveness is much steeper in the neighbourhood of the maximum. The general shape of the curve of sensitiveness is represented by the dotted line in the figure. This was deduced from the formula found applicable to the case of the darkening of other white compounds. It will be seen that the maximum change appears to be effected by the rays of about 0·00045 wave-length, or between F and G.

We are exposing tubes containing known weights of the oxide to the prolonged action of sunshine, with a view to obtain quantitative evidence of the chemical nature of the change.

Crystallography of Phosphorous Oxide.—As first prepared, the oxide is obtained in the cooled condenser in minute crystals, aggregated into a snow-like mass. In the relatively warmer portion of the condenser outside the freezing mixture the oxide is deposited in the feathery forms before referred to. The appearance of these radiating aggregates under a low power of the microscope is seen in Fig. 3. On allowing the melted oxide to cool, it solidifies into thin prisms capped by pyramids; these crystals sometimes attain the length of an inch or more. The character of the crystals is well seen by allowing a drop of the liquefied oxide to solidify under a cover-glass on a microscopic slide, and then partially melting the substance by placing the finger for a moment on the cover-glass. Isolated and well-shaped prismatic crystals, showing many forms, are then seen to rapidly develop, the whole drop ultimately solidifying. If a small quantity of the liquefied oxide is enclosed in a well-stoppered bottle, and turned over so as to wet the walls, and then allowed to drain to the bottom, isolated crystals are formed on cooling. The appearance of these crystals under the microscope, using a magnifying power of about 20 diameters, is shown in the accompanying drawing (Fig. 4). The crystals appear to belong to the monoclinic system, and exhibit the pinacoidal faces $a = \{100\}\infty\bar{P}\infty$ and $b = \{010\}\infty\grave{P}\infty$, several prism faces, a pair of orthodomes, and a pair of complementary pyramidal forms. The extinctions upon a are parallel to the prism edges, whilst those upon b make an angle of about 20° with the prism

FIG. 3.

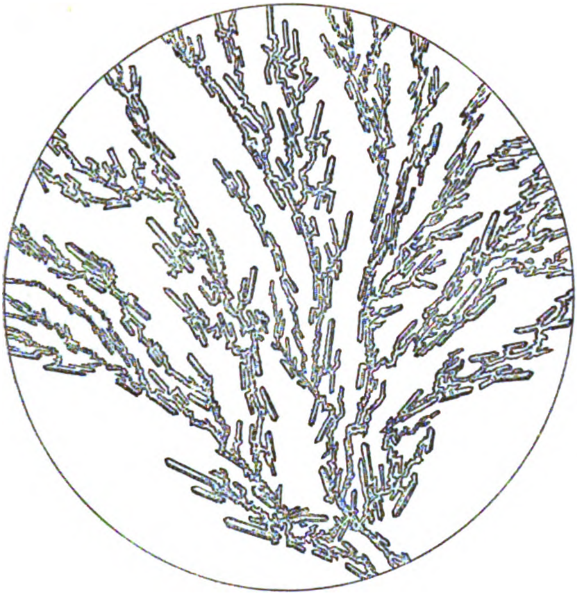
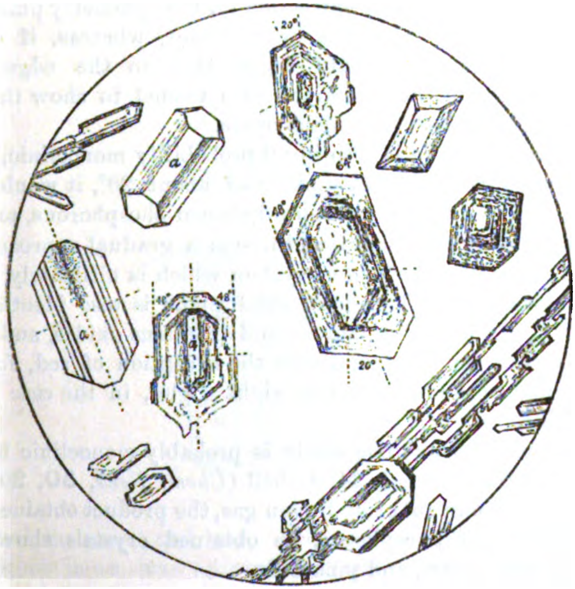


FIG. 4.



edges. In convergent light an optic axis with its system of rings is seen on looking through the orthopinacoid *a* towards the edge of the field in the direction indicated in one of the crystals shown in Fig. 4. When the crossed Nicols are parallel to the axial edges, the brush passes across the centre of the field in a line parallel to the vertical axis. The optic axial plane, therefore, appears to be the symmetry plane *b*.

Goniometrical measurements are impossible in air, owing to the rapidity with which the crystals oxidise and deliquesce. The crystals also, from the low melting point of the oxide, are extremely soft and plastic. The isolated crystals formed by sublimation are similar to those obtained by solidification of the liquid, or from solution in benzene or carbon bisulphide.

No regular crystals of phosphorous oxide have been obtained corresponding to the octahedral forms of arsenious and antimonious oxides. Until recently, the two last-named oxides have been generally regarded as iso-dimorphous. In 1869, Groth (*Pogg. Ann.*, **137**, 414) pointed out the similarity between the crystalline form of the prismatic variety of arsenious oxide and that of valentinite (Sb_4O_6), and concluded that both belong to the rhombic system. Des Cloizeaux (*Compt. rend.*, **105**, 96) adduces evidence in support of the view that arsenious oxide belongs to the monoclinic system, and that this substance is not strictly isomorphous with antimonious oxide, but only homœomorphous, or, to use Groth's term, morphotropic, that is, that the two substances are merely similar in the disposition of their faces. Des Cloizeaux points out that the extinction on the symmetry plane makes an angle of about 6° with the prism edges, whereas, if perfectly rhombic, the extinction should be parallel to the edges. The measurements which were obtained also tended to show the monoclinic nature of prismatic arsenious oxide.

As phosphorous oxide is also in all probability monoclinic, with an extinction upon the symmetry plane of about 20°, it would appear that there is a regular relationship between phosphorous, arsenious, and antimonious oxides, such that there is a gradual approach to the higher symmetry of the rhombic system which is ultimately attained by antimonious oxide. The optic axial plane is also identical with the symmetry plane in phosphorous and arsenious oxides, and also for all the colours of the spectrum, with the exception of red, for which colour the plane crosses to one at right angles, in the case of antimonious oxide.

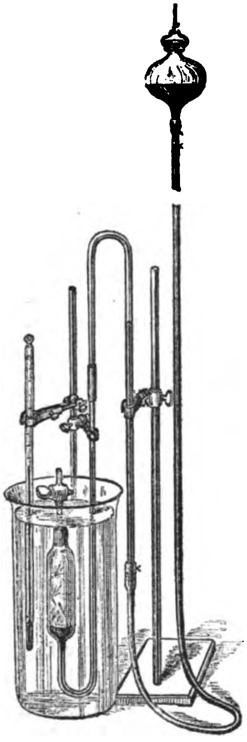
The fact that phosphorous oxide is probably monoclinic has been already surmised by Mr. J. M. Cabell (*Chem. News*, **50**, 209). By resubliming, in a current of hydrogen gas, the product obtained by the slow combustion of phosphorus, he obtained crystals showing the faces of the base, prism, and pinacoids.

Relative Density, Thermal Expansion, and Specific Volume of Phosphorous Oxide.

The relative density of liquid phosphorous oxide was found to be 1·9358 at $\frac{24{\cdot}8^\circ}{4^\circ}$.

An attempt was made to determine the relative density of solid phosphorous oxide, and the amount of contraction in passing from the liquid to the solid state. The apparatus used for this purpose consisted of a dilatometer, the capillary stem of which was bent into a U-shape. The longer limb was about 20 cm. in length and open at the top. The shorter limb carried the cylindrical bulb, which was rather more than 2 c.c. in capacity, and was furnished with a stopcock at its upper end (Fig. 5). The longer capillary limb was graduated in mm., and was calibrated so that the value of the graduations in c.c. was accurately known. Mercury was introduced

FIG. 5.



through the stop-cock until the level in the shorter limb stood just within the bulb. The apparatus was then weighed, the bulb filled with dry carbon dioxide, and the freshly distilled liquid phosphorous oxide introduced by means of a small siphoning arrangement (which precluded the admission of air), until the bulb and neck were filled up to the stop-cock, which was then closed. On again weighing the apparatus, the weight of oxide introduced was known. The arrangement was next placed in a bath of water at about 25°, together with a thermometer, and the temperature of the bath and liquid oxide was slowly reduced by the gradual addition of fragments of ice. The oxide generally remained liquid at 21·5°, and when this temperature was reached, the long graduated limb was almost completely filled with mercury by means of a fine capillary tube. The apparatus was then continually shaken by gentle tapping, and the moment the first sign of crystallisation appeared, the readings of the mercury meniscus and the thermometer were noted. The mercury in the graduated limb rapidly fell, and the tapping was continued until no further depression occurred, when the substance was considered to have wholly solidified. The agitation is very necessary; otherwise, cavities tend to form between the crystals. It was noticed that, on re-melting the solid, a small quantity (about 0·2 c.c.) of gas collected in the upper part of the bulb. This was allowed to escape, and the experiment repeated two or three times, after which, on re-melting, no further evolution of gas was perceived.

The weight of oxide enclosed was 3·5227 grams. In one experiment in which solidification occurred at 21°, a fall of mercury amounting to 146 mm. or 0·153 c.c. was observed. In a second experiment at 21°, when an extra atmosphere of pressure was brought to bear upon the solidifying oxide, a contraction of 155 mm. or 0·163 c.c. was observed. Calculated from the formula for the thermal expansion, 3·5227 grams of liquid phosphorous oxide at 21° occupy 1·813 c.c. If we regard the second experiment as the more trustworthy, 1·813 c.c. contracted to 1·65 c.c. on solidification—a diminution of exactly 9·0 per cent. The relative density of the liquid oxide at $\frac{21^\circ}{4^\circ}$ is 1·9431. The relative density of the solid phosphorous oxide, calculated from the above numbers, is $\frac{3\cdot5227}{1\cdot65} = 2\cdot135$. Owing to the difficulty of ensuring the absence of cavities among the crystals, this value is possibly slightly lower than the truth, but it is probably as good an approximation as the method would enable us to obtain.

The thermal expansion of liquid phosphorous oxide was determined by means of a dilatometer, heated in a glycerine bath, the arrangement of the apparatus and method of observation being similar to that adopted by one of us in determining the thermal expansions of a large number of liquids (compare Trans., 1880). The results of the observations are seen in the following table:—

T. corr.	Dilatometer reading (mm.).	Corr. vol. in c.c.	Relative vol.	Calculated rel. vol.	Diff.
27°·10	13·6	0·7938	1·0000	1·0000	—
36·07	19·7	0·8000	1·0078	1·0078	0·0000
47·66	27·9	0·8084	1·0184	1·0180	0·0004
63·20	38·3	0·8190	1·0317	1·03 6	0·0001
77·06	48·0	0·8290	1·0443	1·0441	0·0002
89·48	57·5	0·8385	1·0563	1·0557	0·0006
103·99	67·8	0·8488	1·0693	1·0693	0·0000
117·68	78·3	0·8594	1·0826	1·0827	0·0001
130·70	89·2	0·8702	1·0962	1·0959	0·0003
140·30	97·3	0·8782	1·1063	1·1058	0·0005

The apparent expansion of phosphorous oxide by heat in glass may be represented by the expression

$$V = 1 + 0{\cdot}0_3 88824t - 0{\cdot}0_6 13873t^2 + 0{\cdot}0_8 38446t^3,$$

by means of which the values in the column headed "Calculated relative volumes" have been obtained. It will be seen from the slight differences shown in the last column that the formula accurately reproduces the original observations.

Correcting for the expansion of the glass (0·0000255) of the dilatometer, the formula becomes

$$V = 1 + 0{\cdot}0_3 91377t - 0{\cdot}0_6 11175t^2 + 0{\cdot}0_8 38607t^3,$$

by means of which the table (p. 560), showing the relative volumes of phosphorous oxide for every 5°, is calculated.

The weight of the oxide in the dilatometer was 1·5338 grams. By calculating the volume of the liquid at 24·8°, the temperature at which the relative density was determined by means of the bottle (*v. supra*), and comparing its weight with that of an equal bulk of water, we can obtain another determination of the relative density at 24·8°. This is found to be 1·9354, a number which is very near that obtained by means of the sp. gr. bottle in which a much larger quantity of a different preparation of phosphorous oxide was employed.

From the above data we obtain 1·6897 as the relative density of phosphorous oxide at its boiling point (173·1°), whence the specific volume $= \dfrac{220}{1{\cdot}6897} = 130{\cdot}2$.

Thermal Expansion of Phosphorous Oxide.

Temperature.	Relative volume.	Difference for 5°.	Temperature.	Relative volume.	Difference for 5°.
25°	1·0000	46	100°	1·0695	49
30	1·0046	45	105	1·0744	48
35	1·0091	46	110	1·0792	49
40	1·0137	46	115	1·0841	50
45	1·0183	45	120	1·0891	50
50	1·0228	46	125	1·0941	51
55	1·0274	46	130	1·0992	51
60	1·0320	46	135	1·1043	52
65	1·0366	46	140	1·1095	52
70	1·0412	47	145	1·1147	53
75	1·0459	47	150	1·1200	54
80	1·0506	47	155	1·1254	54
85	1·0553	47	160	1·1308	55
90	1·0600	47	165	1·1363	56
95	1·0647	48	170	1·1419	
			173·1	1·1454	

A special interest attaches to a knowledge of the specific volume of phosphorous oxide on account of the light it is calculated to throw on the constitution of this substance, and also on the question of the varying sp. vols. of phosphorus dependent on valency. In the paper on Specific Volumes already referred to, one of us gave a number of determinations of the sp. vol. of phosphorus as it exists in combination, both from his own and from other observations up to that time published. The results may be thus summarised:—

Compound observed.	Observer.	Sp. vol. of P.
PCl_3	Pierre	25·4
,, ...	Buff	25·2
,, ...	Thorpe	25·2
PBr_3..............	Pierre	24·1
,, ...	Thorpe	24·0
$POCl_3$	Buff	25·5
,, ...	Thorpe	25·5
$PSCl_3$	Thorpe	25·4
$POBrCl_2$	Thorpe	26·1
$PCl_2C_2H_5O$	Thorpe	25·9

The mean of the 10 estimations for the sp. vol. of P is 25·3. The separate values, of course, depend on a knowledge of the sp. vols. of Cl, Br, O, S, C, and H, and are liable, therefore, to be affected with the errors which exist in those particular values, in addition to the errors which attend the determination of the sp. vols. of the phosphorus compounds. Nevertheless, the agreement among the several values is sufficiently close to leave very little doubt that the sp. vol. of phosphorus in combination is about 25·3. One result which seemed to flow from this conclusion was that, if the sp. vol. of phosphorus in phosphorus trichloride and phosphorus oxychloride was assumed to be identical, the oxygen in the latter compound was united by single linkage, since—

$$\begin{array}{ccc} \text{Sp. vol.} & & \text{Sp. vol.} \\ POCl_3. & - & PCl_3. \end{array}$$
$$101{\cdot}3 - 93{\cdot}4 = 7{\cdot}9,$$

the value of single-linked oxygen being, as Kopp has shown, 7·8, whereas double-linked oxygen is 12·2, a difference of 4·4. This would seem to show that phosphoryl chloride is $P\left\{\begin{array}{l}OCl\\ Cl\\ Cl\end{array}\right.$, which is contrary to the usual mode of representing the constitution of this compound, the chemical evidence, on the whole, tending to show that the chlorine-atoms are of equal value, or in other words, that the phosphorus is pentavalent in phosphoryl chloride. But the physical evidence is apparently borne out by the case of the analogously constituted thiophosphoryl chloride. This compound is found to have the sp. vol. 116·1 and—

$$\begin{array}{ccc} \text{Sp. vol.} & & \text{Sp. vol.} \\ PSCl_3. & - & PCl_3. \end{array}$$
$$116{\cdot}1 - 93{\cdot}4 = 22{\cdot}7,$$

which agrees with Kopp's value of 22·6 for single linked sulphur, double-linked sulphur being 28·6, or a difference of 6·0.

In 1874, Pisati and De Franchis (*Gazzetta Chim. Ital.*, 1874; *Ber. Deut. Chem. Ges.*, 1875, 70) determined the relative density and thermal expansion of phosphorus from 0° up to its boiling point, which they found to be 278·3 under 762 mm. pressure. Their results for liquid phosphorus may be expressed by the formula—

$$V_t = V_{50} + 0{\cdot}0_32969(t - 50) + 0{\cdot}0_62115(t - 50)^2.$$

The variation in relative density is as follows:—

	Solid.		Liquid.
0°......	1·83676	40°......	1·74924
20°......	1·82321	100°......	1·69490
44°......	1·80681	200°......	1·60270
		280°......	1·52867

From these data the sp. vol. of free phosphorus is found to be 20·2.

In 1880, Professors Ramsay and Masson (*Ber.*, 1880, 2147; Trans., 1881, 50) also determined the relative volume of phosphorus at its boiling point, and, as the mean result of four experiments, they found the sp. vol. = 20·91 with a probable error of ± 0·3987.

They discussed the observations on the sp. vol. of phosphorus in combination already referred to, and concluded that the phosphorus in phosphoryl chloride, thiophosphoryl chloride, and phosphoryl bromochloride has the same sp. vol. as it possesses in the free state, and hence, that the values for oxygen and sulphur are respectively those of the double-linked elements, which means that the phosphorus in these compounds is pentavalent. Inasmuch as there can be no question that the sp. vol. of phosphorus in phosphorus trichloride and tribromide, in which phosphorus is trivalent, is about 25, it would seem to follow that the sp. vol. of phosphorus varies with its valency, as H. L. Buff, as far back as 1865 (*Annalen Suppl.*, **4**, 129), supposed.

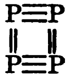
Our observations on the sp. vol. of phosphorous oxide lend additional support to the view that the sp. vol. of phosphorus varies either with its valency, or with its mode of atomic grouping. If we assume that all the oxygen-atoms in phosphorous oxide have the minimum value 7·8, or, in other words, that they are united by single linkage, *the sp. vol. of phosphorus in phosphorous oxide is found to be* 20·9, *which is exactly the value found for phosphorus in the free state:*

$$\text{Sp. vol. P} = \frac{\text{Sp. vol. of } P_4O_6 - \text{sum of sp. vols. of single-linked oxygen-atoms}}{\text{Number of atoms of P in mol. of } P_4O_6},$$

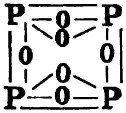
$$\text{or sp. vol. of P} = \frac{130{\cdot}2 - (6 \times 7{\cdot}8)}{4} = 20{\cdot}9.$$

It will be obvious that if any of the oxygen-atoms are double-linked, that is, possess the higher value 12·2, the value for the sp. vol. of phosphorus will be lower than 20·9. Hence, 20·9 is the maximum value possible. And the further result would seem to follow that the phosphorus-atoms in phosphorous oxide have the same valency as in free phosphorus, and that in both these substances the phosphorus-atoms are pentavalent.

Pisati and Nasini (*Ber.*, **21**, 2155; Abstr., 1888, 1027) have attempted to determine the molecular weight of phosphorus by Raoult's method in a benzene solution, and their results indicate that the molecule of dissolved phosphorus is at least made up of not more than 4 atoms, which accords with the deductions from the vapour-density determinations at temperatures up to 1040°. Beckmann (*Zeit. physikal. Chem.*, **5**, 76—82; Abstr., 1890, 447) has also adduced evidence dependent on the influence of dissolved phosphorus on the boiling point of carbon bisulphide to show that the molecular weight of phosphorus in solution corresponds with the molecule P_4. Hence, if the phosphorus-atoms in the molecule of free phosphorus are pentavalent, it follows that the phosphorus molecule must be regarded as possessing a closed-chain constitution, thus :—



and since phosphorous oxide is, apparently, to be regarded as made up of pentavalent phosphorus-atoms combined with single-linked oxygen-atoms its constitution would be written—



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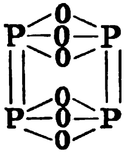
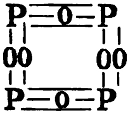


or



There are, however, certain difficulties in the way of these general conclusions. Phosphoryl chloride is assumed to contain pentavalent phosphorus because it is directly transformed into orthophosphoric acid by the action of water. Now, since phosphorus trichloride, which must be supposed to contain trivalent phosphorus is transformed by a similar reaction into phosphorous acid, that acid must also be assumed to contain trivalent phosphorus. But as will be shown hereafter, phosphorous oxide by hydration also passes into phosphorous acid, which would seem to indicate that phosphorous oxide also contains trivalent phosphorus-atoms, which is opposed to the result just arrived at. All that the experimental data warrant us in concluding is, that phosphorus in combination may, like oxygen, sulphur, and possibly nitrogen, have a variable specific volume, and we venture to think that we may claim to be the first to have established that fact unequivocally from the example of phosphorous oxide; but whether the variable specific volume is in any way connected with the variable affinity values of phosphorus is as yet an open question. This hypothesis has not been proved to explain the variable sp. vol. of the other elements above named. Buff, more than five-and-twenty years ago, attempted, but unsuccessfully, to trace the intradependence of these two variables. The aromatic hydrocarbons have invariably a lower sp. vol. than that calculated from Kopp's values deduced from hydrocarbons of the paraffin series and their derivatives, but there is here no case of variable valency. The conclusion, therefore, to which we come is, that the variation in the sp. vol. of phosphorus may be related to the atomic arrangement of the phosphorus-atoms in the molecule of the element and in that of the phosphorous oxide, both of which molecules contain in all probability the same number of phosphorus-atoms, but that it is not necessarily dependent upon the variation in combining power of the element.

Refraction Equivalent of Phosphorous Oxide. Determination of Refractive Index.

As is well known, the researches of Gladstone and Dale, Landolt, Brühl, Van t'Hoff, and others have enabled them to deduce certain general relations between the optical properties of substances and their chemical constitution. Moreover, Brühl and, independently, Gladstone have traced connections between the refractive powers of substances and their specific volumes.

Inasmuch as phosphorous oxide is easily obtained pure, and when melted forms a clear, transparent liquid, it became of interest to determine its refractive index with a view of comparing its refraction equivalent with that of other phosphorus compounds. It was thought that the observations would have all the more importance from the circumstance that the question as regards the phosphorus compounds in particular is extremely complicated, and hence additional data are greatly needed. We have, therefore, taken very special pains to make our determinations as accurate and as complete as possible, in the hope that if we ourselves were unable to unravel their indications, the data might be found useful to subsequent inquirers.

The spectrometer employed was a large instrument made by Aug. Becker, of Göttingen, and was kindly lent to us by Professor Bedson; with the aid of two micrometers, placed 180° apart, the circle could be read to 2″ of arc, and the last second could easily be estimated.

The observations were made in a room of which the temperature was maintained at a few degrees above the melting point of phosphorous oxide, the limits being 26·5° and 28·2°. The phosphorous oxide was redistilled directly into the hollow glass prism of about 60° angle; this was previously filled with carbon dioxide, and was fitted with a good stopper. The lines observed were the red lithium, yellow sodium D, the green thallium, and the three brightest hydrogen lines, $H\alpha$, $H\beta$, and $H\gamma$, corresponding to C, F, and G of the solar spectrum. Two independent series of observations were made with different preparations of the oxide. In each series four pairs of readings were taken for each line, and in the second series, after one set of readings had been taken, the observations were repeated with the prism rotated in azimuth, so as to receive the incident rays upon the second face. In order to obtain a general expression for the refraction of phosphorous oxide of the form given by Cauchy—

$$\mu = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} + \ldots,$$

where μ is the refractive index, and λ the wave-length of the particular ray employed, the observations were combined so as to form two sets of three equations of condition, the values for the three metallic lines forming one set, and those of the three hydrogen lines the other. The equations were independently solved for the constants A, B, and C, and the mean of these values taken. The general expression for the refraction of liquid phosphorous oxide at the temperature 27·4° is thus found to be—

$$\mu = 1{\cdot}5171 + \frac{817670}{\lambda^2} - \frac{316590\,000\,000}{\lambda^4} + \ldots\ldots$$

The following table shows the results of the actual observations, and the values of the refractive index calculated by the above formula:—

Table showing the Refractive Index of Phosphorous Oxide.

Line observed.	Wave-length.	Mean angle of min. dev.		μ obs.		μ calc.	Diff.
		I Series.	II Series.	I Series.	II Series.		
Lithium red........	6705	39° 45′ 52″	40° 14′ 26″	1·5350	1·5349	1·5352	0·0003
Hydrogen red (C) ..	6562	39 50 9	40 19 35	1·5358	1·5360	1·5359	0·0000
Sodium yellow (D)..	5892	40 14 23	40 44 04	1·5403	1·5405	1·5405	0·0001
Thallium green	5348	40 41 06	41 10 28	1·5454	1·5453	1·5453	0·0000
Hydrogen green (F).	4861	41 14 59	41 45 24	1·5518	1·5517	1·5512	0·0005
Hydrogen blue (G)..	4340	42 07 34	42 38 11	1·5616	1·5614	1·5596	0·0019

It will be seen that the formula reproduces the observations with great exactness, the greatest divergence being in the case of hydrogen γ which is confessedly the most difficult of measurement. The values of μ as given are reduced to a vacuum. The actual experimental numbers were in all cases 0·0004 less. The angle of the prism during the first series of observations was 59° 34′ 05″, and during the second series 60° 0′ 48″.

In calculating the refraction equivalent, that is, $\frac{\text{mol. wt.} \times (\mu - 1)}{\text{relative density}}$, μ is generally made to represent the refractive index either for the line A of the spectrum or for a ray of infinite wave-length. The calculated value of μ for line A of the spectrum (wave-length 7604) for phosphorous oxide is 1·5311. The value for a ray of infinite wave-length is the constant A in the general expression for the refraction, viz., 1·5171

The relative density of liquid phosphorous oxide at the mean temperature of the refraction observations is 1·9300. The refraction equivalent of phosphorous oxide for the line A of the spectrum is—

$$\frac{220 \times 0{\cdot}5311}{1{\cdot}93} = 60{\cdot}5.$$

For the ray of infinite wave-length it is—

$$\frac{220 \times 0{\cdot}5171}{1{\cdot}93} = 58{\cdot}9.$$

If the oxygen is represented by its lowest value, corresponding to single-linked oxygen, which for the line A is 2·9, and for a ray of infinite wave-length 2·8; the values of the phosphorus in phosphorous oxide are 10·8 for line A, and 10·5 for a ray of infinite wave-length. If any of the oxygen-atoms are doubly linked, corresponding to the higher values 3·4 or 3·3, the value of the phosphorus becomes, of course, slightly less; in the extreme case it would be 10·0.

Gladstone and Dale have shown that the refraction equivalent of free phosphorus referred to the line A is identical with the value it has in phosphorus trichloride and tribromide. This value is about 18. On the other hand, in phosphoryl chloride, metaphosphoric and orthophosphoric acids, the value is much lower, viz., about 8. It is impossible in the light of our present knowledge to explain these results or to bring them in line with the deductions from the specific volume observations. The differences are, of course, far too large to be accounted for by any possible experimental errors.

It is remarkable that a substance so rich in phosphorus as phosphorous oxide should have such a comparatively low refractive power.

Dispersion of Phosphorous Oxide.

The refractive index for the line H (wave-length 3969) is 1·5677, as calculated from the general formula above given. The length of spectrum, $\mu_H - \mu_A$, is 1·5677 − 1·5311 = 0·0366. The dispersion equivalent as expressed by the formula—

$$\text{Mol. wt. } \frac{\mu_H - \mu_A}{\text{density}}$$

$$\text{is} = \frac{220 \times 0{\cdot}0366}{1{\cdot}93} = 4{\cdot}17.$$

The difference between the length of spectrum of phosphorous oxide and of free phosphorus is very striking. In the case of free phosphorus, the rays about the line A are absorbed, but the length from C to H_1, that is $\mu_{H_1} - \mu_C$, is as much as 0·1679, the value of μ for the line C at 40° being 2·0677, and for line H_1 2·2356 (Dale and Gladstone, *Phil. Trans.*, 1863, 320). It is remarkable that the combination of phosphorus with oxygen not only reduces the refractive index from 2·1 to 1·5, but also reduces the dispersive power to such an extent that the length of the spectrum is diminished from more than 0·1679 to 0·0366.

Magnetic Rotation of Phosphorous Oxide.

Dr. Perkin, who kindly offered to make the necessary observations, has furnished us with the following determinations of the magnetic rotation of phosphorous oxide:—

"The magnetic rotation of phosphorous oxide gave the following numbers:—

	"*t.*	Sp. R.	Mol. R.
	24·5°	1·5916	10·013
	24·5	1·5865	9·981
	24·5	1·5844	9·967
	24·5	1·5844	9·967
	24·5	1·5856	9·975
	25·0	1·5795	9·941
	25·0	1·5780	9·931
	25·0	1·5765	9·921
	25·0	1·5826	9·960
	25·0	1·5829	9·961
"Average	24·75	1·5832	9·962

"The magnetic rotatory power of phosphorus compounds has not been much studied as yet, but from the results which have been obtained, phosphorus in the free state is found to have a much larger rotation than when in combination with oxygen, as in the ethyl phosphates and phosphites.

"The above results show that this is also the case with phosphorous oxide, where the influence of this element is apparently not very much higher than in triethyl phosphite."

Action of Water on Phosphorous Oxide.—Phosphorous oxide is generally supposed to possess a great affinity for water. Most text-books state that it rapidly deliquesces in air, and instantly dissolves in water with a hissing noise. According to Gmelin (*Handbuch der Chemie*), "the anhydrous acid attracts the moisture of the air with so great a development of heat that it takes fire." In reality pure phosphorous oxide is somewhat inert in its attraction for water.

Both the solid and the liquid form dissolve only with great slowness; a few grams will remain for several days in contact with water without any considerable diminution in bulk being apparent. On long standing, the pure oxide completely dissolves; the solution has a strong acid reaction and an alliaceous smell; it reduces mercuric chloride to calomel, and throws down metallic silver from silver nitrate solution. It has no action on copper sulphate solution on boiling, nor does it reduce iodates or liberate iodine from potassium iodide solution; hence it seems to form phosphorous acid by gradual assimilation of water. 1·3703 grams of freshly distilled phosphorous oxide were sealed up in a glass tube with about 5 c.c. of distilled water which had previously been boiled and then allowed to cool in an atmosphere of carbonic acid. The tube and contents were allowed to stand in the dark for five weeks, at the end of which time the solid had almost entirely disappeared. The slight residue which remained proved to be free phosphorus; after drying in a stream of carbon dioxide, it weighed 0·014 gram, or 1·02 per cent. The filtered solution was then mixed with excess of mercuric chloride solution and warmed to 60°, and the precipitated calomel collected and weighed. The actual amount of phosphorous acid in the solution, assuming that it reduces mercuric chloride to calomel in accordance with the equation—

$$H_3PO_3 + 2HgCl_2 + H_2O = Hg_2Cl_2 + H_3PO_4 + 2HCl,$$

was thus found to be 2·0021. The phosphorous oxide taken (after deducting the 0·014 of free phosphorus) should yield 2·0221 H_3PO_3, on the supposition that it combined with water according to the equation—

$$P_4O_6 + 6H_2O = 4H_3PO_3.$$

The concordance of the numbers is sufficiently close to show that phosphorous oxide is slowly converted into phosphorous acid by the action of cold water.

When a small quantity of water, not lower than 15° in temperature, is added to a quantity of phosphorous oxide, not less than one-sixth its bulk, the slight rise of temperature (due to the formation of phosphorous acid?) at the surface of contact is just sufficient after about 10 minutes to melt the oxide which remains unmixed with the water at the bottom of the vessel. This slowly dissolves, as above described, and in a few days forms a solution of phosphorous acid.

When the water is heated, the reaction is entirely different. At temperatures below 100° it is very energetic; large quantities of red phosphorus or the red suboxide are formed with an explosive evolution of spontaneously inflammable phosphoretted hydrogen and the formation of phosphoric acid. With quantities of phosphorous oxide exceeding a couple of grams, hot water produces most violent explosions.

Action of Caustic Alkalis.—Cold dilute solutions of caustic soda or potash resemble cold water in their action on phosphorous oxide. No action is apparent at first, but, on standing, the oxide is dissolved, and a phosphite is formed. Cold concentrated or hot dilute solutions decompose the oxide with production of red phosphorus, or the red oxide P_4O, and a phosphate, whilst spontaneously inflammable phosphoretted hydrogen is evolved.

Action of Ethyl Alcohol.—Although phosphorous oxide is so slowly acted on by water at ordinary temperatures, it instantly ignites in contact with absolute alcohol. By cooling the oxide, and allowing the absolute alcohol to fall drop by drop upon it, the reaction may be easily controlled, when it is found to occur in accordance with the equation:—

$$P_4O_6 + 8C_2H_6O = 4P\begin{cases}OC_2H_5\\OC_2H_5\\OH\end{cases} + 2H_2O.$$

The *diethyl phosphorous acid* so formed is a colourless liquid of a penetrating, garlic-like smell boiling at 184—185°, and having a relative density of 1·0749 at $\frac{15\cdot5^\circ}{4}$. Further details of the mode of preparation and properties of this compound are reserved for a subsequent communication.

Ether, *carbon bisulphide*, *benzene*, and *chloroform* dissolve phosphorous oxide without change.

Action of Oxygen.—Phosphorous oxide spontaneously oxidises to phosphorus pentoxide on exposure to air or to oxygen. A small quantity of the oxide in a test-tube in contact with the air soon becomes surrounded by a voluminous deposit of the pentoxide, which deliquesces at the margin nearest the mouth of the tube. When a few decigrams of phosphorous oxide are placed at the bottom of a wide tube closed at one end, and previously filled with dry oxygen, and the tube sealed and kept in the dark, in an upright position, a bulky, snow-like deposit of pure phosphoric oxide is formed in rhythmic striæ or annuli along the walls of the tube, showing that vaporisation of the phosphorous oxide precedes its oxidation. The action is comparatively slow at first, but seems to proceed at an accelerated rate as the tension of the included oxygen diminishes, whereby the volatility of the phosphorous oxide is increased. Under diminished pressure, the tube is seen to be more or less filled with a luminous fluctuating glow, which instantly stops when the tension is increased to atmospheric pressure. By increase of temperature, effected by warming the outside of the tube with a water-jacket, the diminution of pressure required to produce the glow becomes less—a further proof that the glow is due to the action of oxygen on the *vapour* of phosphorous oxide. If the temperature is gradually raised to about 70°, the rate of volatilisation, and consequent oxidation, is such that the mass of phosphorous oxide burns, but the vigorous combustion can be at once stopped by reducing the pressure of the oxygen, and immediately renewed by restoring the pressure, and the experiment can be repeated until the whole of the oxide or the oxygen is used up.

The change from glow to actual flame is perfectly regular and gradual, and is unattended with any sudden increase in brilliancy. In this respect, the process of oxidation is analogous to the slow and barely visible burning of fire-damp which is sometimes seen to occur in the Davy lamp, or to the slow combustion of ether and other vapours which has been specially studied by Dr. Perkin. No ozone is formed as the oxidation proceeds. This fact is important, as it seems to support the assumption that the formation of ozone during the glow of phosphorus is caused by the dissociation of the oxygen molecule in the formation of phosphoric oxide—

$$\begin{aligned} P_2 + 3O_2 &= P_2O_5 + O, \\ O + O_2 &= O_3. \end{aligned}$$

When phosphorous oxide is converted into the pentoxide, no dissociation of oxygen molecules need be assumed to occur—

$$P_4O_6 + 2O_2 = 2P_2O_5.$$

A good method of showing the glow of phosphorous oxide for lecture purposes is to pour a solution of the oxide in carbon bisulphide on to filter-paper wound round a test-tube; the tube with its moistened coating of paper is then introduced into a wider tube about twice its length, one end of which is drawn out and closed with a stopcock, the other end being fitted with a cork also carrying a stopcock. A stream of hydrogen is then passed through the outer tube until the carbon bisulphide has evaporated. The tube is now attached at one end to a vacuum-reservoir, and at the other to an oxygen supply. On exhausting the tube, the finely divided phosphorous oxide on the paper begins to glow; on restoring the pressure from the oxygen supply, the glow at once stops.

These phenomena are so very similar to those which occur with phosphorus alone that it might be thought that the glow observed in the case of phosphorous oxide is due to the presence of free phosphorus in that compound. The amount of free phosphorus required to produce a glow is so very small that the supposition cannot be at once dismissed as impossible. We can only say that every sample of the oxide we have tried has always showed the glow even after repeated distillation, treatment with metallic copper, &c. Nor have we been able to perceive any difference in the extent of the glow or in the conditions under which it occurs with different preparations. The absence of the ozone and the gradual increase in the intensity of the glow, until it passes into steady combustion as the temperature is increased, seem to us convincing that phosphorous oxide phosphoresces in contact with oxygen like phosphorus itself, and under very similar conditions. Moreover, no hydrogen peroxide could be detected when the glow occurred in moist air, whereas the glow of phosphorus under the same conditions is attended with the production of notable quantities of that substance.

Melted phosphorous oxide readily takes fire in the air, especially when gently warmed or when spread out over the surface of paper or cloth. Thrown into oxygen heated to 50° or 60°, it instantly ignites with a flame of almost blinding brilliancy. On the completion of one of the determinations of vapour-density by the Hofmann method, the apparatus having cooled, a measured quantity of oxygen was introduced into the tube, the temperature of which was slowly raised by surrounding it with steam. The room being darkened, a series of some half-dozen brilliant flashes of flame extending throughout the whole length of the gaseous column was observed. No violent oscillation of the mercury column was perceptible; hence, neither the temperature of ignition nor the heat of combination was very high. The amount of oxygen consumed was close upon that required to form P_2O_5.

It will be obvious, therefore, that great care is necessary to exclude air from the apparatus during the process of distillation of phosphorous oxide. If air is permitted to enter the distilling vessel, the vapour of the oxide at once ignites, and may set fire to the liquid, with the possibility of a dangerous explosion. It is necessary, therefore, to keep a continuous and sufficiently rapid stream of dry carbon dioxide playing round the mouth of the receiver.

Action of Ozone on Phosphorous Oxide.—A tube was fitted with platinum wires, like an Houzeau's ozone-tube, in such manner that a slow stream of oxygen passing through it could be ozonised by the silent discharge, and the ozonised oxygen was passed over a small quantity of phosphorous oxide placed within the tube. Under these circumstances, the phosphorous oxide glowed continuously, that is, without the remarkable pulsating appearance which characterises its glow in air or in oxygen under diminished pressure. The glow ceased when the silent discharge was interrupted, but recommenced immediately it was resumed. The glow in the case of the ozonised oxygen (which, of course, was at the ordinary atmospheric pressure) was close to the oxide, and not, as in the case of air, or in rarefied oxygen, at some distance away from it. Moreover, after a time, owing apparently to the energy of the reaction, the phosphorous oxide melted, whereas it never melts in pure oxygen or in air at the ordinary temperature.

Action of Chlorine.—Phosphorous oxide thrown into a jar of chlorine instantly ignites, and burns with a greenish flame. In a slow current of dry chlorine, the oxide becomes very hot, and burns with a pale green flame scarcely perceptible in daylight. If the flask containing the phosphorous oxide is surrounded by ice, and the current of chlorine is not too rapid, the whole of the oxide is gradually converted into a clear liquid which does not solidify in cold water. On distilling this liquid, the thermometer rises rapidly to 107°, and remains constant at this temperature for some time, after which it suddenly rises to 200°, and the residue in the flask becomes viscid. This residue is the so-called metaphosphoryl chloride, PO_2Cl, of Gustavson, obtained by heating $POCl_3$ and P_2O_5 together. The action of chlorine on phosphorous oxide may be represented by the equation—

$$P_4O_6 + 4Cl_2 = 2POCl_3 + 2PO_2Cl.$$

In an actual experiment, 7·46 grams P_4O_6 yielded 10·54 grams $POCl_3$ and 6·68 grams PO_2Cl. According to the above equation, the amount of phosphorous oxide taken should have yielded 10·41 grams $POCl_3$ and 6·68 grams PO_2Cl.

Theory indicates the possible existence of two modifications of phosphoryl chloride, $Cl_2P{\cdot}OCl$ and $Cl_3P{:}O$, but all attempts to obtain isomeric modifications of this substance have hitherto failed. Michaelis and La Coste (*Ber.*, **18**, 2118) have, however, drawn attention to the fact that isomeric derivatives corresponding to the two oxychlorides are known, viz.:—

III.		V.
$(C_6H_5)_2P{\cdot}O{\cdot}C_6H_5$	and	$(C_6H_5)_3P{:}O$
Phenoxyldiphenylphosphine.		Triphenylphosphine oxide.

The first-named compound is a thick, oily liquid, readily acted on by bromine, oxygen, sulphur, and selenium, and yields crystallisable addition-products with the alkyl haloïds; whereas the latter is a solid, melting at 153·5°, on which the above-named substances have no action.

In view of the possible existence of isophosphoryl chloride, we submitted the oxychloride obtained by the action of chlorine upon phosphorous oxide to a careful examination. It was found to boil constantly at 107·0° (corr.), and its sp. gr. was 1·7119 at 0°. The boiling point of the oxychloride obtained from phosphorus pentachloride by the action of phosphoric pentoxide was formerly found by one of us (Trans., 1880, 338) to be 107·22° (corr.), and its sp. gr. 1·71185 at 0°. Hence the oxychloride obtained from phosphorous oxide is identical with that obtained from phosphoric oxide.

Phosphorous oxide has a well-marked physiological effect, and it is not improbable that the action hitherto attributed to phosphorus itself, especially as regards its influence on the glycogenic function of the liver and on tissue change may be really due to this substance. It is well known that persons employed in the manufacture of lucifer matches are occasionally attacked by caries of the lower jaw. This is not due to the action of the phosphorus after absorption into the circulation, but to the direct effect of the fumes upon the bone itself. For it has been found that when a bone of an animal fed by phosphorus was exposed, no carious change took place; but if one were exposed to the fumes, caries was produced, and amongst lucifer-match makers it has been noticed that only those who have carious teeth suffer from necrosis of the jaw (Lauder Brunton, "Pharmacology, &c.," 771). The fumes from phosphorus consist largely of phosphorous oxide; by drawing air over phosphorus without allowing it to ignite, and passing the fumes through a narrow strongly-cooled tube, a deposit is obtained which melts with the warmth of the hand, and gives the reactions for phosphorous oxide. Moreover, the odour of the product is identical with that of pure phosphorous oxide, and it is also identical with the peculiar smell noticed in a lucifer-match manufactory during the making and handling of the "composition" with which the splints are tipped, and which is present in the neighbourhood of the benches where the "boxers" are at work. It is highly probable, as Schönbein (*Pogg. Ann.*, **75**, 377) long ago surmised, that phosphorus vapour, as such, is odourless, and that the smell which phosphorus ordinarily possesses is a mixture of that of ozone and of phosphorous oxide.

We are continuing the study of this compound, and have already investigated the action upon it of ammonia, sulphur, sulphuric acid, the chlorides of phosphorus, &c. And we are also engaged in experiments on its behaviour with a number of organic substances. We hope to be able to lay the results of our work before the Society at an early date. It gives us much pleasure to acknowledge our indebtedness to Mr. Barker North, Assoc. N.S.S., for his assistance in the preparation of the phosphorous oxide which has served for the present investigation.

XXXV.—*An Investigation of the Conditions under which Hydrogen Peroxide is formed from Ether.*

By Professor **Wyndham R. Dunstan** and **T. S. Dymond**.

It has been asserted by various chemists, from the time of Schönbein to the present day, that an oxidising substance, either ozone or hydrogen peroxide, is formed when ether is exposed to light. Berthelot has stated that hydrogen peroxide is produced when ozone acts on ether in presence of water. It also appears that a substance possessing oxidising properties is generated during the slow combustion of ether, but the evidence as to the precise nature of this substance is unsatisfactory.

Three years ago (*Pharm. J.*, **17**, 841), we communicated to the Pharmaceutical Society an account of some experiments we had made on the behaviour of light towards pure ether, from which we concluded that neither ozone nor hydrogen peroxide is produced under these circumstances. Since then we have fully substantiated this conclusion by another series of experiments, of which an account is given in this paper, and having extended the inquiry, we are now in a position to state precisely the conditions that are necessary in order that hydrogen peroxide may be formed from pure ether.

I. *Action of Light on Ether.*

The statement that ozone is produced when ether is exposed to light seems to have been first recorded by Schönbein (*J. Chem. Soc.*, **4**, 134) in a paper communicated to this Society, in which he draws attention to the fact that ether which has been exposed to light and air contains a substance possessing powerful oxidising properties; this substance he believed to be either ozone or a body isomeric with it. Ether deprived of air and kept in the dark was found not to yield this substance. This statement has, on Schonbein's authority, been assumed to be true, and during the last fifty years it has been repeatedly made, the oxidising action being attributed by some writers to ozone, and by others to hydrogen peroxide; but the experimental investigation of the subject has been carried very little, if any, further than the stage at which it was left by Schönbein (*cf.* Kingzett, Trans., **37**, 805; *Chem. News*, **34**, 135; Warden, *Pharm. J.*, **15**, 521; Buchner, *Chem. Zeit.*, **9**, 69; Werner, *Pharm. J.*, **16**, 660). None of these observers has adduced experimental proof that the oxidising substance, whether ozone or hydrogen peroxide, is actually derived from the ether and not from an impurity contained in it.

Recently the subject has again attracted attention, owing to the experiments of Berthelot (*Compt. rend.*, **108**, 543), who has recorded results which, in his judgment, are sufficient to prove that hydrogen peroxide may be formed from ether by the action of air and water at ordinary temperatures. The ether employed in some of these experiments had been purified by washing it with lime-water. The hydrogen peroxide was detected by means of its reaction with chromic acid. According to Berthelot, the formation of the hydrogen peroxide is dependent, in the first instance, on the previous production of ethyl peroxide by the direct action of oxygen; this compound being decomposed by water with formation of hydrogen peroxide. Berthelot had already shown that ethyl peroxide may be prepared by the action of ozonised air on ether, and that it is decomposed by water to form hydrogen peroxide. He now assumes that at ordinary temperatures atmospheric oxygen is also competent to produce ethyl peroxide from ether, but the experiments he describes in support of this assumption seem to us to be unsatisfactory. Berthelot has made these results the basis of a theory as to the mode in which plants assimilate atmospheric nitrogen. He finds that during this slow aërial oxidation of ether that traces of nitrites are produced at the expense of the atmospheric nitrogen, which is supposed to be oxidised by the ethyl peroxide or by the hydrogen peroxide, but the experimental evidence for this theory is not conclusive. It is doubtful whether Berthelot regards light as a necessary condition of reaction between ether and oxygen.

In a paper lately communicated to this Society by Dr. Arthur Richardson, it is again asserted that wet ether forms hydrogen peroxide when exposed to light, and he offers an entirely new explanation of the manner in which the hydrogen peroxide is produced. Richardson claims to have proved that the hydrogen peroxide is derived, not from the ether, but from the combination of oxygen with water under the influence of light; in point of fact, that the water, not the ether, is oxidised. The action of the ether is merely to promote the stability of the hydrogen peroxide, and to enable it to accumulate in the liquid, an effect which, it is alleged, may also be brought about by the addition to the water of sulphuric acid instead of ether; water thus acidified is stated to form hydrogen peroxide when exposed to light in contact with air. It would appear, however, that Richardson does not attach importance to the question of the purity of the ether, since no allusion is made to it in the published abstract of his paper (Proc., 1889, 134).

Still more recently, Poleck and Thümmel (*Ber.*, **22**, 2863; *Arch. Pharm.*, 1885, 918) have investigated this subject. The ether they employed was purified by shaking it with aqueous sulphurous acid and afterwards with milk of lime. The ether was then dried and distilled from phenylhydrazine. Ether thus purified, when exposed to sunlight and air, either wet or dry, was found to yield hydrogen peroxide together with a substance which is supposed to be vinyl alcohol, the action being represented by the equation $(CH_3CH_2)_2O + O_3 = 2(CH_2{\cdot}CHOH) + H_2O_2$. The hydrogen peroxide acting on ether is stated to form more vinyl alcohol, $3(CH_3CH_2)_2O + 9H_2O_2 = 6CH_2{\cdot}CHOH + 12H_2O + O_3$. It would be out of place for us to criticise here the remarkable conclusions, chiefly with reference to the production of vinyl alcohol, which are set forth in this paper. It is only necessary to point out that the method of purifying ether adopted by the authors would serve to remove only such compounds as are attacked by sulphurous acid or combine with phenylhydrazine, and are more soluble in water than in ether.

A consideration of the papers published by Berthelot, Richardson, and by Poleck and Thümmel shows that, while all these observers assert that hydrogen peroxide may be formed from ether under ordinary atmospheric conditions, they do not agree as to the precise circumstances which are necessary for its formation, and each attributes the alleged effect to a different cause. Berthelot regards ether, oxygen, and water as necessary factors in the reaction which results in the oxidation of the ether to ethyl peroxide and the subsequent decomposition of this compound by water to form hydrogen peroxide. Richardson considers that only the oxygen and water react under the influence of light, and that the ether takes no part in the chemical change. Poleck and Thümmel do not regard the presence of water as a necessary condition of the reaction, ether, oxygen, and light alone being required, and their interpretation of the change is diametrically opposed to that offered by Berthelot and also to that suggested by Richardson, which are likewise opposed to each other.

We believe that this extraordinary conflict of opinion, as well as of experimental evidence, is mainly the result of the different degrees of impurity of the ether employed by these observers. Apparently they have not suspected that the formation of hydrogen peroxide might be due to an impurity in the ether; at any rate, the means they adopted to purify the compound are insufficient to exclude the possibility that this may be the case.

Moreover, none of these observers alludes to a paper published by us in 1887 (*Pharm. J.*, **17**, 841), in which are recorded the results of an experimental enquiry into the nature and mode of formation of the substance possessing oxidising properties, which is sometimes observed to occur in ether. At the time when this enquiry was commenced, we found that this substance had been variously stated to be ozone or hydrogen peroxide. Within that year a paper had been published in which it was asserted that ozone exists in the liquid, but no conclusive evidence of the nature of the oxidising substance had hitherto been adduced. It is, of course, highly improbable that ozone can exist in presence of ether.

A specimen of ether was procured which possessed oxidising properties, and liberated iodine from potassium iodide. It had been prepared from methylated spirit and was manifestly impure. When this ether was shaken for a few seconds with mercury and then removed from contact with the metal, it was still found to liberate iodine from potassium iodide. Had ozone been present, the mercury would at once have destroyed it. The oxidising properties of the ether were immediately destroyed by warming it with aqueous alkali, and the escaping gas contained no ozone. After prolonged agitation with mercury, the ether no longer acted on potassium iodide. These results pointed to the absence of ozone and to the presence of hydrogen peroxide. Conclusive evidence of the existence of hydrogen peroxide in the liquid was obtained by the formation of the blue compound with chromic acid.

Experiments were next made on the mode of formation of the hydrogen peroxide, particularly with reference to its formation from pure ether. Ether prepared by the reaction of alcohol and sulphuric acid was employed after purification by repeated agitation with potash solution and with water. The relative density of this specimen was 0·730 and its boiling point 35°. A small quantity of the ether was placed in a large colourless bottle and exposed to daylight for two months. No hydrogen peroxide was formed, and the ether did not act on a dilute solution of potassium iodide. The experiment was repeated with a mixture of ether and water, but again no hydrogen peroxide resulted. In order to determine whether oxygen has any action on ether, 8 litres of air were very slowly passed through 200 c.c. of the ether, but no substance capable of reacting with potassium iodide was formed. The experiment was repeated, using warm ether saturated with water, but again no effect was produced. In another experiment, oxygen was slowly passed through ether saturated with water, and heated to 30° while it was exposed to light. More than 200 litres of oxygen were employed. No iodine-liberating substance was produced. Lastly, an experiment was made in which ether and water acidified with dilute sulphuric acid were used, but again a negative result was obtained.

These results, published by us in 1887, are directly contradictory of those published in 1889 by Berthelot, by Richardson, and by Poleck and Thümmel.

During the course of these experiments, we observed that some specimens of ether, prepared from alcohol and sulphuric acid and purified by the usual method, especially after they had been kept for some time, were able to act slowly on aqueous potassium iodide. The total amount of this action was small, and it was proved not to be occasioned by the presence of hydrogen peroxide, since the ether did not react with chromic acid and the effect was not appreciably diminished by agitation with silver oxide, whereas a dilute ethereal solution of hydrogen peroxide is instantly decomposed by contact with this reagent. At first we were inclined to believe that Ferrière's contention (*J. Pharm. Chim.* [4], **16**, 107) is correct, and that pure ether actually possesses the power of decomposing aqueous potassium iodide, since this specimen had been carefully purified and its relative density and boiling point were those of the pure liquid. Further investigation showed, however, that Ferrière's conclusion is erroneous, since it was observed that not only did different specimens, preserved under the same conditions, vary in respect of the amount of their action on potassium iodide, but that ether prepared by the reaction of sodium ethoxide with ethyl iodide did not liberate iodine. It appeared, therefore, that there must be present in the ether a minute quantity of some impurity formed during the preparation of ether by the ordinary method.

At this time we were prevented by the pressure of other work from pursuing the subject further, but at the beginning of last year we determined to continue the enquiry by repeating some of the experiments we had previously made, and attempting to rid ether of the minute amount of impurity to which we have referred.

The results of the second series of experiments, now to be described, leave no room for doubt that pure ether does not form hydrogen peroxide when exposed to light and air in presence either of water or of diluted sulphuric acid.

Three different specimens of ether were subjected to the action of daylight. They had been prepared and purified in the following manner.

Ether prepared by the reaction, under pressure, of excess of sodium ethoxide with ethyl iodide. The product was thoroughly washed with water, dried, and distilled.

Ether prepared by the reaction of alcohol and sulphuric acid, purchased as "pure ether," was further purified by agitating it successively with a small quantity of sulphuric acid, potash solution, and water. After having been dried over solid potash it was distilled.

Ether prepared from methylated spirit was purified in exactly the same manner as the previous specimen.

Of the three specimens thus prepared and purified, the first two did not in the least affect a one per cent. solution of potassium iodide or react with dilute chromic acid. The third specimen afforded a very pale yellow colour with dilute potassium iodide, which was somewhat intensified by the addition of very dilute sulphuric acid, but it did not afford evidence of the slightest trace of hydrogen peroxide when tested with chromic acid.

We have ascertained the delicacy of the characteristic reaction of hydrogen peroxide with chromic acid, and have compared its delicacy with the potassium iodide reaction. 20 c.c. of a solution containing 0·00125 gram of hydrogen peroxide in 100 c.c. of the liquid were mixed with a few drops of a dilute solution of chromic acid (prepared by the addition of dilute sulphuric acid to a one per cent. solution of potassium dichromate), and shaken with 20 c.c. of ether. The ether separated from the liquid of a pale-blue colour, distinctly recognisable. With more dilute solutions, the blue colour was only indistinctly seen. The reaction is thus shown to be capable of revealing the presence of 0·00025 gram of hydrogen peroxide.

In testing ether for hydrogen peroxide, care has to be taken not to add a large excess of chromic acid, since this seriously impairs the delicacy of the reaction. One or two drops of the one per cent. solution of potassium dichromate, acidified with dilute sulphuric acid, should be added to about 20 c.c. of water, and the liquid shaken with about an equal volume of the ether. If the yellow colour of the aqueous liquid disappears, a little more of the chromic acid must be added. It is important to observe that the *ethereal layer* which separates is blue, and not merely the aqueous liquid, since the presence in the ether of an easily oxidisable substance will lead to the reduction of the chromic acid and to the formation of a greenish-blue solution of a chromium salt. 20 c.c. of the solution in which the hydrogen peroxide had been recognised by the reaction with chromic acid were now mixed with an equal volume of ether and the same quantity of a one per cent. solution of potassium iodide. After a few seconds, a pale-yellow colour was observed, which deepened on the addition of dilute sulphuric acid. The chromic reaction for hydrogen peroxide is more satisfactory than that with potassium iodide, since it is instantaneous; a dilute neutral solution of hydrogen peroxide acts only very slowly on a solution of potassium iodide, and acidified potassium iodide, although it reacts more rapidly, cannot, under the present circumstances, be relied on as a test for hydrogen peroxide, since certain organic compounds are attacked by hydriodic acid.

About 100 c.c. of each of the above-mentioned three specimens of ether, saturated with water, were placed in an almost colourless (faintly greenish) "Winchester quart" bottle (holding about 3 litres), and exposed to daylight for two months, during August and September, so that the ether was subjected to much sunlight. The temperature varied

Action of Light on Ether.

No. of specimen.	Mode of preparation and purification.	Reactions.	Reactions after two months' exposure to daylight.	Reactions after three months' exposure to daylight.	Reactions after five months' exposure to daylight and two months (3 hours nightly) to electric arc light.
1......	Prepared from EtI; purified by KOH	KI (1 p. c.), none HI (1 p. c.), none H_2CrO_4, none	none none none	none none none	none. none. none.
2......	Prepared from meth. spirit; purified by H_2SO_4, KOH, H_2O	KI, light yellow HI, do. H_2CrO_4, none	deep yellow orange pale blue	deep yellow dark orange blue	deep yellow. red. blue.
3......	Prepared from alcohol; purified by H_2SO_4, KOH, H_2O.	KI, none HI, faint yellow H_2CrO_4, none	none faint yellow none	none faint yellow none	faint yellow. yellow. none.
					Reaction after exposure to daylight, and three hours nightly to electric arc light during two months.
4......	Prepared from meth. spirit; purified by HI, $Na_2S_2O_3$, KOH, H_2O	KI, none HI, none H_2CrO_4, none	— — —	— — —	none. faint yellow. none.
5......	Prepared from meth. spirit; purified by H_2CrO_4, $NaHSO_3$, KOH, H_2O	KI, none HI, none H_2CrO_4, none	— — —	— — —	none. none. none.

Action of Light on Ether—continued.

No. of specimen.	Mode of preparation and purification.	Reactions.	Reactions after two months' exposure to daylight.	Reactions after three months' exposure to daylight.	Reactions after exposure to daylight, and three hours nightly to electric arc light during two months.
6......	Prepared from alcohol; purified by H_2CrO_4, $NaHSO_3$, KOH, H_2O	KI, none HI, none H_2CrO_4, none	— — —	— — —	none. none. none.
7......	Same as 6 (without air)	KI, none HI, none H_2CrO_4, none	— — —	— — —	none. none. none.
8......	Same as 6 (without light)	KI, none HI, none H_2CrO_4, none	— — —	— — —	faint yellow. none. none.
9......	Same as 6 (without water)	KI, none HI, none H_2CrO_4, none	— — —	— — —	none. none. none.
10......	Same as 6 (with water + 1 p. c. H_2SO_4)	KI, none HI, none H_2CrO_4, none	— — —	— — —	none. none. none.

between 15—25°. At the end of this time, each specimen was tested with (1) one per cent. aqueous potassium iodide, (2) the same acidified with dilute sulphuric acid, and (3) dilute chromic acid. The results are recorded in the accompanying table (preceding pages). The ether prepared from sodium ethoxide and ethyl iodide did not react with any of the reagents; that prepared from alcohol and sulphuric acid was also unchanged, but the specimen prepared from methylated spirit now contained hydrogen peroxide. The exposure to light was continued for another month, when the specimens were again tested. The ether prepared from ethyl iodide and from alcohol were still unchanged; the specimen prepared from methylated spirit had developed more hydrogen peroxide, and now liberated much iodine from potassium iodide, and yielded a fine blue colour with chromic acid. These experiments prove that pure ether mixed with water and exposed to light does not develop hydrogen peroxide. Under the same conditions, ether prepared from methylated spirit, purified by the usual process, and subsequently with sulphuric acid and potash, does develop hydrogen peroxide. The results obtained by us in 1887 are thus confirmed.

It seemed possible, however, that sunlight in London, deprived to a large extent, as it frequently is, of ultra-violet rays, might possibly be incompetent to produce the effects that have been recorded by previous observers. We therefore decided to ascertain the result of exposing pure ether to the electric arc light. We also wished to discover whether ether prepared from methylated spirit could be purified from the substance which causes the formation of hydrogen peroxide, and whether the minute amount of iodine-liberating substance could be removed from ether prepared in the usual manner. For this purification two reagents seemed particularly well adapted, namely, hydriodic acid and chromic acid; both these substances slowly decompose pure ether, especially when concentrated.

A specimen of ether prepared from methylated spirit and purified in the manner already described was agitated with half its volume of a four per cent. solution of hydriodic acid. Iodine was liberated at once and abundantly. The treatment was continued until little immediate action occurred. The ether was shaken with aqueous sodium thiosulphate to remove free iodine, then with potash solution, and finally with water. Another portion of the same specimen of ether was purified by repeated agitation with a four per cent. solution of potassium dichromate acidified with sulphuric acid. Chromic acid of this strength acts very slowly on pure ether, but immediately attacks the impure liquid. The chief product of the action of chromic acid on ether is aldehyde, and in case any of this substance might have been formed, the ether, after it had been separated from the chromic acid, was agitated with a solution of sodium hydrogen sulphite, then with water, potash solution, and finally again with water. We have alluded to the circumstance that some specimens of ether prepared from alcohol, and purified in the usual manner, were found to exert a feeble action on potassium iodide, especially after they had been kept for some time, not necessarily in the light. A specimen of such ether was now purified with chromic acid in the manner above described.

These three specimens (numbered 4, 5, and 6 in the table), saturated with water, were exposed during two months to daylight, and each evening to a large electric arc light for a period amounting, on an average, to three hours nightly. The Winchester bottles containing about 100 cubic centimetres of each specimen were placed on a level with the arc light at a distance of about 1 yard. The temperature varied from 10—15°. At the same time the three specimens (numbered 1, 2, and 3) whose behaviour during a three months' exposure to daylight has already been discussed, were subjected to the same treatment, as were also three other specimens (numbered 7, 9, and 10) prepared from alcohol and purified with chromic acid. One of these specimens (numbered 7), saturated with water, was contained in a small bottle, which it completely filled, so that air was absent; the second specimen (numbered 9) was completely dried by prolonged contact with, and distillation from metallic sodium; the third specimen (numbered 10) was mixed with water containing one per cent. of sulphuric acid. All these liquids were exposed to daylight as well as to the electric light, and with the exception of 7 were contained in "Winchester quart" bottles of almost colourless glass. Another specimen of the same ether (numbered 8), saturated with water, was kept in the dark. There was also exposed to light with the specimens of ether a quarter of a litre of pure water acidulated with one per cent. of pure sulphuric acid, in order to determine whether, as has been alleged, hydrogen peroxide is formed under these circumstances.

The results of the examination of these specimens after two months' exposure to daylight and electric light are recorded in the table (p. 581).

The ether prepared from ethyl iodide did not react with potassium iodide, hydriodic acid, or with chromic acid.

The ether prepared from methylated spirit contained an increased amount of hydrogen peroxide.

The ether prepared from alcohol and purified with sulphuric acid and potash reacted faintly with potassium iodide, and decidedly with hydriodic acid, but not with chromic acid. These three specimens had now been exposed to daylight for five months, and during two months to the electric light for three hours nightly, but no hydrogen peroxide had formed in those derived from ethyl iodide and from alcohol; that prepared from methylated spirit alone contained hydrogen peroxide. With respect to the other specially purified specimens, in no case had hydrogen peroxide been formed, neither had it formed in the acidulated water. It is therefore proved that the substance capable of yielding hydrogen peroxide may be removed from impure ether by the action either of hydriodic acid or of chromic acid. It is also proved that the addition of dilute sulphuric acid to pure ether does not promote the formation of hydrogen peroxide, and that this substance is not produced when oxygen and dilute sulphuric acid are exposed to light.

We consider that the results now recorded conclusively demonstrate that hydrogen peroxide cannot be formed from purified ether by exposing it to light, under ordinary atmospheric conditions, in contact with air and water. The results recorded by former observers must have been due to the employment of impure ether. Since some of these observers appear to have worked with what is ordinarily known as "pure ether," which presumably is not prepared from methylated spirit, it would seem that occasionally ether prepared from alcohol, if not purified in the manner we have described, is liable to contain a substance which develops hydrogen peroxide.

We have not been able to ascertain the nature of this impurity, owing to the circumstance that it is present, together with other substances, in very small quantity. Of the impure specimens of ether we have examined, that which was richest in hydrogen peroxide had been for many years exposed to light. It contained only 0·04 per cent. of hydrogen peroxide as determined by its iodine-liberating power in an acid solution.

II. *Action of Ozone on Ether.*

Berthelot has observed (*Ann. Chim. Phys.* [5], **27**, 229; *Compt. rend.*, **86**, 71) that when ozone is passed into ether, ethyl peroxide is formed, and that this compound reacts with water to produce hydrogen peroxide. Since Berthelot has given no information respecting the purity of the ether he used, it seemed to be important to ascertain whether ozone reacts with pure ether in this manner. Through a quantity of pure ether a current of ozonised oxygen was passed; the escaping gas possessed little, if any, of the characteristic smell of ozone. After the passage of the gas had been continued for some hours, the ether was shaken with water. On the addition of dilute chromic acid to the mixture, the ether separated of a magnificent blue colour, showing that a considerable quantity of hydrogen peroxide had been produced.

It appears probable that ether, like turpentine, is capable of absorbing the whole molecule of ozone, but we have not further investigated this question, since Mr. Shenstone has expressed a wish to deal with it in connection with the investigation he is making of the properties and reactions of ozone prepared from pure oxygen.

III. *The Slow Combustion of Ether.*

It is well known that when ether is heated with a limited supply of air, a pungent, highly irritating substance is produced which has been called "lampic acid." Legler (*Ber.*, **14**, 602; *Annalen*, **217**, 381) has investigated the nature of the products formed under these circumstances. He obtained, besides formic aldehyde and other compounds, a crystalline substance to which he assigned the formula $C_{11}H_{33}O_{21}$. It possesses oxidising properties, but it is doubtful whether Legler actually obtained hydrogen peroxide from its decomposition,* and apparently he did not find this substance among the products of the combustion. Perkin (Trans., 1882, 363) has drawn attention to the character of the flame which is observed when ether undergoes this change, and he mentions that aldehyde is formed, but no allusion is made to hydrogen peroxide.

In our first experiments on this point, air was drawn through pure ether slightly warmed, and the air charged with ether vapour was passed into a tube containing pumice heated to low redness. A lambent flame or glow was observed within the tube. The escaping vapours were condensed in cold water. This aqueous liquid, which possessed a highly pungent odour and taste, contained no hydrogen peroxide; it did not react either with potassium iodide or with chromic acid. Aldehyde and acetic acid were the chief products of the action. Other experiments were made with oxygen instead of air, and the same result was obtained. Further observations were made with a form of apparatus in which opportunity was afforded for the immediate condensation of any hydrogen peroxide that might be formed. About 50 c.c. of pure ether were placed in a large flask, together with about the same quantity of water. A glass rod heated to low redness was repeatedly introduced into the upper part of the flask, so that it locally heated the air immediately above the liquid. The contents of the flask were agitated from time to time, so that any hydrogen peroxide that might be formed would be dissolved by the cold water. This process was continued until nearly the whole of the ether had disappeared. The remaining liquid contained much hydrogen peroxide; it liberated iodine from potassium iodide, and afforded a fine blue colour with chromic acid. It was found that the most convenient form of apparatus for producing hydrogen peroxide by the slow combustion of ether consists of a modified Döbereiner's lamp, to which fresh supplies of air could be constantly admitted. A large flask, containing enough ether to cover the bottom and about an equal quantity of water, is connected with a wash-bottle containing cold water. Through the cork of the flask there passes a wide tube, open at both ends, through which air is admitted, a spiral of stout platinum wire, and an elbow tube which is joined to the wash-bottle. By means of an aspirator connected with this bottle, a current of air is drawn through the wide tube into the flask. The spiral is heated to redness and plunged into the flask, the current of air being so regulated that the platinum is maintained at a low red heat. From time to time the flask is shaken. Hydrogen peroxide is continuously formed, and when the ether has nearly disappeared, a considerable quantity will be found in the remaining water, while some can be detected in the water of the wash-bottle. In this process of oxidation, although the oxygen of the air is almost entirely consumed, little or no carbon dioxide is produced. The simplest interpretation of the change appears to be that the reaction is similar to that which occurs when ozone reacts with ether in presence of water. At a low red heat the ether forms a peroxidised product which is decomposed by water with the production of hydrogen peroxide. It seems to be unnecessary to suppose that the atmospheric oxygen is actually ozonised before it peroxidises the ether. The alternative hypothesis is that under the conditions of the experiment water is directly oxidised, but there is no experimental justification for this view. We find that neither water nor dilute sulphuric acid forms hydrogen peroxide when heated with air in the manner above described, and we have likewise failed to observe its formation during the evaporation of water in air.

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* In the abstract of Legler's paper which appeared in this Journal (Abstr., 1881, 576), it is erroneously stated that the compound reacts with alkalis to form hydrogen peroxide. Legler states that hydrogen is formed.

We have not been able to form hydrogen peroxide by the slow combustion of acetone, alcohol, ethylene, or coal gas.

Summary.

Hydrogen peroxide is not formed when pure ether is exposed to light in contact with air either in presence or absence of water.

Some specimens of ether, notably those prepared from methylated spirit, develop hydrogen peroxide when kept, unless they have been previously purified by repeated treatment with dilute chromic acid.

Ozone reacts with pure ether, and the product, when mixed with water, yields hydrogen peroxide.

The imperfect oxidation of pure ether effected by locally heating it in air leads, when water is present, to the production of hydrogen peroxide.

Hydrogen peroxide is not formed by the action of light on water and oxygen even in presence of dilute sulphuric acid; neither is it produced under similar conditions when the oxygen or the water is heated.

Research Laboratory,
Pharmaceutical Society of Great Britain.

XXXVI.—*Note on the preparation of Pyrocatechol.*

By W. H. Perkin, Jun., Ph.D.

In the course of some experiments on derivatives of pyrocatechol, my attention was drawn to the high price of this substance (Kahlbaum's price is 4*s.* for 10 grams), and it appeared very desirable to endeavour to find some method by which this important product might be readily and cheaply prepared. Although this phenol is so expensive, its methyl ether guaiacol can be obtained for 20*s.* per kilo. and less; and experiments were therefore instituted with the object of ascertaining whether, under suitable conditions, a good yield of pyrocatechol might be obtained from guaiacol.

Baeyer (*Ber.*, 8, 153) has shown that pyrocatechol may be obtained by saturating guaiacol, heated at 195—200°, with hydrogen iodide, and fractionating the product, but the yield obtained is small. By slightly modifying the conditions, that is, by using a solution of hydrogen iodide instead of the gas, I have found that an almost quantitative yield of pyrocatechol may be readily obtained.

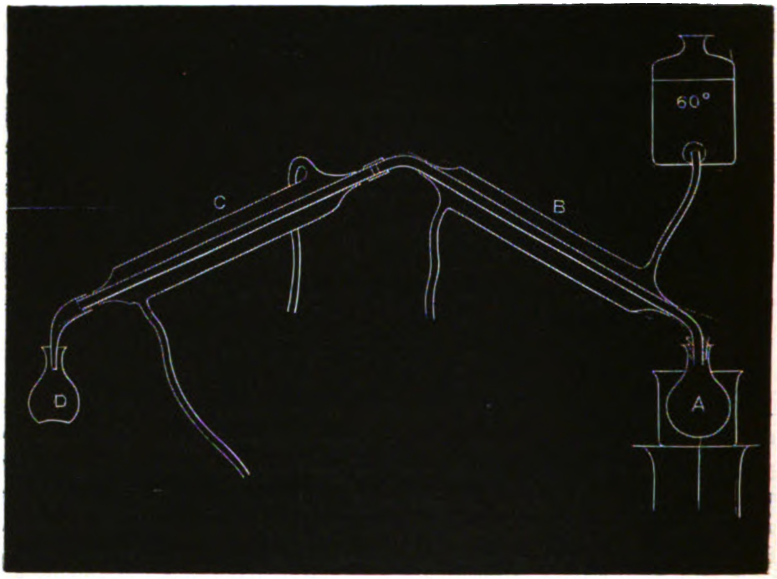
The details of this method will be readily understood with the help of the following sketch of the apparatus employed, which was suggested by that of the one described by Zeisel for use in his experiments on the determination of methoxyl-groups (*Monats.*, 6, 995).

A is a flask of about 750 c.c. capacity, suspended in an oil- or glycerol-bath.

B is a condenser through which water, heated to 60°, is allowed to circulate.

The condenser C is kept well cooled with water.

At the commencement of the operation a solution of 100 grams of guaiacol in 150 grams of fuming hydriodic acid (sp. gr. 1·96) is placed in the flask A, which is then fitted firmly to the condenser B, and very gradually heated to boiling. In a short time abundance of methyl iodide is given off, and this, after passing through B, condenses in C, and collects in the flask D, which should contain a little water and be kept cold. The mixture is gently heated for one hour, allowed to cool slightly, mixed with more hydriodic acid (50—75 grams), and heated as before for one hour. It was found that 101 grams of slightly moist methyl iodide had distilled over, whereas theory requires 114 grams.



The product of the reaction was mixed with three times its volume of water, extracted six times with ether, the ethereal solution washed with a little water, decolorised with a little sulphurous acid, and dried over calcium chloride The ether was then distilled off, and the residual dark-coloured oil purified by rapid fractionation. As soon as the last traces of ether had passed over, the thermometer rose at once to 230°, between which temperature and 255° the whole distilled as a colourless oil which, on cooling, solidified to a hard cake of crystals of pyrocatechol. The yield obtained was 85 grams or 96 per cent. of the theoretical.

In order to further purify this product, it was melted, poured into 100 c.c. of boiling benzene, and the solution allowed to stand over night. The crystals were drained, washed with a little benzene, dried on a porous plate over sulphuric acid, and analysed with the following result:—

0·1749 gram substance gave 0·0900 gram H_2O and 0·4211 gram CO_2.

	Theory. $C_6H_4(OH)_2$.	Found.
C	65·45	65·60
H	5·45	5·72
O	29·09	28·68

The substance melted at 104°, and possessed all the properties of pyrocatechol.

The crystals obtained weighed 63 grams, without taking into account what remained in the mother liquor.

While engaged on this subject, experiments were made on the action of hydrochloric acid on guaiacol. As, however, guaiacol is almost insoluble in hydrochloric acid, simple boiling did not appear to produce much effect on the oil; but decomposition readily sets in if the liquids are heated together under pressure. 30 grams of guaiacol and 50 c.c. of ordinary concentrated hydrochloric acid were heated in a sealed tube for four hours at 170—180°. The tube, after cooling, was wrapped in a cloth, inverted, the capillary inserted into a flask, and broken at the tip; in this way the whole contents were readily transferred to the flask; otherwise, owing to the pressure in the tube and the tendency of the liquid to froth, loss can scarcely be avoided.

The product was mixed with water, extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the residual oil fractionally distilled. Almost the whole quantity passed over between 230° and 255° as a colourless oil which solidified completely on cooling, and consisted of almost pure pyrocatechol. This method could no doubt be successfully carried out in digesters, and if the yield is as good as when hydriodic acid is used, pyrocatechol should be readily made at comparatively small cost.

Heriot Watt College,
Edinburgh.

XXXVII.—*Nitrogen Trioxide and Peroxide.*

By W. Ramsay, Ph.D., F.R.S.

In 1888, I showed that the molecular weight of liquid nitrogen tetroxide at about 17° corresponded to the formula N_2O_4, as determined by the lowering of the freezing point of dry acetic acid. The numbers obtained varied between 90·3 and 95·9; the calculated molecular weight of N_2O_4 being 92 (Trans., **53**, 621).

The present paper treats of (1) the preparation of the tetroxide; (2) the preparation of the trioxide; (3) the physical properties of the tetroxide—its melting point, its molecular lowering of melting point, and its heat of fusion; (4) the molecular weight of the trioxide, determined by the lowering of the melting point of the tetroxide by dissolved trioxide; and (5) some of the properties of the trioxide.

1. *Preparation of the Tetroxide.*—The well-known method of distilling arsenic trioxide with nitric acid yields a green liquid consisting of a variable mixture of tetroxide and trioxide. The equation $As_2O_3 + 2HNO_3 = 2HAsO_3 + N_2O_3$ doubtless expresses the fundamental change which occurs. But the trioxide, being incapable of existence as gas, splits into peroxide, NO_2, and nitric oxide, NO, and, on condensation, part of the peroxide condenses as tetroxide, N_2O_4, while nitric oxide escapes. The reaction is further modified by the decomposing action of the water of the nitric acid on the trioxide. And, lastly, the nascent trioxide may be supposed to react with nitric acid, thus:—$2HNO_3 + N_2O_3 = 2N_2O_4 + H_2O$. But this reaction yields water, which exerts a decomposing action on the peroxide and on the trioxide. The general result of all these simultaneous actions is, therefore, to yield a mixture of peroxide and nitric oxide, which partly combine to form trioxide on condensation.

If sulphuric acid be added, so as to withdraw water, the yield of peroxide is increased, but much of the nitrogen remains in combination with the sulphuric acid in some such form of combination as hydrogen nitrosyl sulphate, which is not readily decomposed by heat in presence of excess of strong oil of vitriol. The yield is, therefore, a poor one.

The process may be modified by heating a mixture of arsenic trioxide and sulphuric acid to about 200° in a retort, and adding strong nitric acid very slowly through a separating funnel, the tube of which passes to the bottom of the retort; each drop occasions a brisk evolution of peroxide, which distils over. But here a curious colour-change occurs for which I am unable to suggest an explanation. The first few drops of nitric acid change the contents of the retort to a dark blue-green colour; the addition of a little more converts the green into orange-red, and peroxide is evolved. If time be given for the evolution of bubbles to cease, the colour-change may be again produced.

By this means a pure orange-red liquid may be produced which merely requires distillation to be perfectly pure peroxide. The yield here is also disappointing, for much nitrogen remains with the sulphuric acid.

An easier method of preparation is to procure the blue-green liquid, consisting of trioxide and peroxide, by the usual method of distilling arsenic trioxide and nitric acid, and then to add it to a mixture of strong nitric acid with a large quantity of phosphorus pentoxide, care being taken to keep the nitric acid cold with ice during the gradual addition of the pentoxide. On adding to this mixture the blue liquid, and shaking, the colour changes at once to orange. The reaction obviously takes place:—

$$N_2O_5 + N_2O_3 = 2N_2O_4.$$

It is thus easy to convert trioxide into tetroxide. The tetroxide is poured away from the syrupy mixture and distilled. The same mixture of phosphorus pentoxide and nitric acid may be used again and again to convert fresh quantities of trioxide into tetroxide.

2. *Preparation of the Trioxide.*—The trioxide of nitrogen cannot be obtained pure. It is easily produced by passing a current of nitric oxide into cold tetroxide. The mixture soon turns dark blue, and then consists of a mixture of tetroxide and trioxide. It was shown by Mr. Cundall and myself (Trans., **47**, 677) that the first portions of gas boiling off such a mixture have the composition expressed by the formula N_2O_3, and that this mixture possesses the density calculable for such a mixture in molecular proportions of $NO + (NO_2 + N_2O_4)$. The liquid remaining after a quantity of this mixture had been distilled off was green in colour, and approximated closely in composition and density to $(NO_2 + N_2O_4)$.

3. *Physical Properties of the Tetroxide*—(*a.*) *Melting Point.*—The melting point of nitrogen tetroxide is given as −9° by old observers; Deville and Troost (*Compt. rend.*, **64**, 257) give it as −10°. As a mean of four concordant experiments, in two of which different samples were employed, the supercooled liquid rose to −10·14° on solidification; the temperature given by Deville and Troost is, therefore, substantially accurate.

(*b.*) *Molecular Depression of Melting Point.*—This constant is ascertainable from the depression in the melting point of nitrogen tetroxide, produced by dissolved substances. Two experiments were made in which chlorobenzene and chloroform were employed. These are among the few available and unobjectionable substances which are not acted on by nitrogen tetroxide. Owing to the ease with which nitric peroxide attacks cork and indiarubber, their presence had to be avoided. The apparatus consisted of a small bottle of about 30 c.c. capacity, into which a delicate thermometer, arbitrarily graduated, but in which each division of the scale corresponded to rather more than a tenth of a degree, was ground, to serve as a stopper. The range of this thermometer was between +5° and −20°. It was standardised by comparison with a special thermometer, constructed by Müller, of Bonn, the accuracy of which had been ascertained by using it to determine the vapour pressures of water at low temperatures. As the scale of the standard thermometer did not show temperatures below −4°, lower temperatures on the thermometer with arbitrary degrees, were obtained by extrapolation. It was often very difficult to cause the tetroxide to freeze. The bottle, with weighed contents, was cooled in a dry test-tube, placed in a freezing mixture of crushed ice and hydrochloric acid, the temperature of which was often as low as −27°: and it was usually only after the most vigorous shaking that solid formed, and the temperature rose to the melting point. It often happened, in spite of the thermometer serving as a stopper fitting the bottle as well as grinding could make it, that leakage occurred on shaking, and the experiment had to be again begun. It was impossible to use a lubricant, because all such substances are attacked by nitrogen tetroxide.

Having ascertained the freezing point of the peroxide before each experiment, an approximately measured volume of chloroform or of chlorobenzene was added, and thermometer and bottle again weighed. The details of the two experiments are as follows:—

I. Tetroxide taken, 17·3046 grams.

Chloroform added, 0·5269 gram = 3·045 per 100 N_2O_4.
Freezing point, −11·2°; depression − 1·06°.
Depression for 1 part of chloroform per 100 of tetroxide, 0·35°.
Depression per molecule chloroform, 0·35 × 119·4 = 41·0°.

II. Tetroxide taken, 16·7650 grams.

Chlorobenzene added, 0·4931 gram = 2·941 parts per 100 N_2O_4.
Freezing point, −11·23°; depression, 1·09°.
Depression for 1 part of chlorobenzene per 100 of tetroxide, 0·37°.
Depression per molecule chlorobenzene, 0·37 × 112·4 = 41·66°.

The molecular depression may, therefore, be taken as 41.

Raoult found, in many of his experiments, that the molecular depression, divided by the molecular weight of the solvent, gave a constant approximating to 0·63.

This number was obtained with formic and acetic acids, with benzene, with nitrobenzene, and with ethylene bromide; but not with water. And it must be remembered that but few solvents have been experimented with.

The molecular depression of nitrogen tetroxide, therefore, divided by 0·63, should approximate to its molecular weight, if this substance agrees with the majority of those investigated by Raoult. Applying this rule, we have 41/0·63 = 65. This number does not agree with the molecular weight of the tetroxide, as determined by myself in 1888; and the want of concordance led me to suspect the accuracy of the determinations with chloroform and chlorobenzene.

But instead of repeating such determinations, a better check is obviously suggested by the following considerations:—

The heat of fusion of a substance may, according to Van't Hoff (*Phil. Mag.* [5], **26**, 88), be calculated from the molecular depression of its freezing point by dissolved substances. Let T be the freezing point of the solvent, t the molecular depression, and W the heat of fusion; then

$$W = \frac{0{\cdot}02T^2}{t}.$$

Substituting for T, 262·86°, the freezing point of the tetroxide on the absolute scale, and for t, 41·0, the molecular depression, we have—

$$W = \frac{0{\cdot}02 \times 69094}{41} = 33{\cdot}7 \text{ calories.}$$

Now, if the heat of fusion, determined directly, corroborates this calculated number, it proves, indirectly, the correctness of the molecular depression, and affords a check on the anomaly, whereby the quotient 41/0·63 = 65 is obtained instead of 92, the true molecular weight.

Heat of Fusion of Nitrogen Tetroxide.—The method of ascertaining this constant was the usual one. A weighed amount of tetroxide was placed in the small bottle before mentioned, the stopper of which was a delicate thermometer. The tetroxide was then frozen and transferred to a calorimeter, the fall of temperature of the water being noted. The specific heat of the liquid was ascertained by noting the fall of temperature produced on placing the bottle containing a known weight of liquid tetroxide in the calorimeter. The capacity for heat of the bottle was then ascertained; and from two experiments of the kind an estimation was made of the specific heat of the solid tetroxide.

The last datum is difficult to determine with accuracy; I have considered it sufficient to show that it does not materially affect the results.

The numerical data are as follows:—

(1.) Total heat—

	I.	II.
Tetroxide taken.........	7·9315 grams	7·5635 grams.
Rise of temperature.....	33·04°	32·23°
Heat absorbed..........	428·5 cals.	402·0 cals.
Heat capacity of bottle ..	0·212 cal. per degree.	

(2.) Specific heat of liquid detroxide—

	I.	II.
Tetroxide taken	7·9315 grams	7·9315 grams.
Rise of temperature.....	22·29°	16·48°
Total heat per degree of N_2O_4 and bottle	−3·964 cals.	−3·753 cals.

Deducting capacity for heat of bottle, and dividing by weight,

Specific heat of liquid tetroxide,	0·4730	0·4464
Mean....................	0·46	

(3.) From the total heat, the heat capacity of the liquid tetroxide is subtracted—

It amounts to..................	84·6 cals.	81·2 cals.
Also heat capacity of bottle	7·2 „	6·8 „
The remainder is	336·7 „	314·0 „

The specific heat of the solid tetroxide may be formed by a simultaneous equation; it is approximately 1·0. But this number is obviously too high; moreover, the probability of its being correct is very small, because it is obtained from the difference between the temperatures −19·98° and −19·03°. Assuming its correctness, however, the heat of fusion of the solid tetroxide is 32·6. The number calculated from the molecular lowering of the temperature is 33·7; and the agreement is a very close one. Supposing, however, that the specific heat of the solid were identical with that of liquid, viz., 0·46, the heat of fusion would be 38·0 from the first experiment, and from the second, 36·4 calories. To take an extreme case: suppose the specific heat of the solid to be zero, the heat of fusion would be, in the first case, 42·4, and in the second, 41·5 calories.

Now, let us apply the last extreme supposition to the molecular depression of the melting point of the solid tetroxide, in order to see whether, on the hypothesis that the heat of fusion is 42 calories, a quotient such as Raoult found, viz., 0·63, can be obtained. The formula will become—

$$x = \frac{0{\cdot}02 \times 69094}{42} = 33,$$

when x is the molecular depression of the freezing point; and dividing 33 by 0·63, the molecular weight of the peroxide would be 52, instead of the number found, 65. This, it is seen, is a still less probable result, when the other evidence in favour of the molecular weight 92 for the tetroxide is considered, viz., its colour, its vapour-density, and, lastly, my previous determinations where acetic acid was employed as solvent. Nitrogen tetroxide, therefore, appears to be another exception to the rule that the quotient obtained by dividing the molecular depression by the molecular weight is 0·63. It would be interesting to study this point further, but nitrogen tetroxide is hardly the substance which one would select for experiment, as such determinations are exceedingly difficult, and demand no ordinary patience and skill.

4. *The Molecular Weight of Nitrogen Trioxide.*—There appears to be no reason to reject, as a solvent, a substance which shows abnormal results such as those of nitrogen tetroxide. Many valuable determinations of molecular weights have been made with the use of water as solvent, though the molecular weight of water itself, determined by the help of other solvents, leads to very abnormal and contradictory results. Hence, an attempt was made to determine the molecular weight of nitrogen trioxide by dissolving a known weight of the latter in nitrogen tetroxide (or rather, by converting a known weight of tetroxide into trioxide by means of a current of nitric oxide), and then ascertaining the depression in the freezing point of the tetroxide caused by the addition.

This solvent offers peculiar advantages. I have made previous attempts to determine the molecular weight of the trioxide by using perfectly dry acetic acid as solvent; but with no avail, for the trioxide is so unstable that it decomposed during the experiment. But as the tetroxide is one of the products of dissociation of the trioxide, if it is possible to determine the constant in any way, this is the obvious one; for, in presence of tetroxide, the trioxide attains its greatest stability. Moreover, the freezing point of the tetroxide is so low that the stability of the trioxide is favoured.

This constant is peculiarly interesting in view of Dr. Thorpe's recent discovery, that the corresponding compound of phosphorus, like those of arsenic and antimony, is represented by the formula P_4O_6, and not by P_2O_3, as formerly supposed. It is true that nitrogen does not belong to the same vertical row of the periodic table as phosphorus; yet the compounds of these two elements show much similarity; and the peroxide of nitrogen polymerises into the tetroxide; hence, it appeared possible that the so-called trioxide might really turn out to be tetranitrogen hexoxide.

The method of preparing the trioxide was to pass a current of dry nitric oxide through a weighed amount of the tetroxide contained in a cooled U-tube, until the colour became dark blue. The U-tube was then sealed, allowed to gain the temperature of the laboratory, and then weighed. From the gain in weight, the amount of N_2O_3 in solution was calculated. The U-tubes and experimental bottle were then cooled to −20°; the contents of the U-tube were transferred to the bottle, and the U-tube was again sealed and weighed. That the composition is really that expressed by $N_{2n}O_{3n}$, is proved by analyses by Gay-Lussac, by Tritsche, and by Péligot, besides by the analysis of first portions of distillate, by Mr. Cundall and myself, previously referred to. Hence, the determinations to be given really decide the molecular weight of this substance, and not that of nitric oxide, which, of course, can also be deduced from them.

The numerical results are as follows:—

	I.	II.	III.
	grams.	grams.	grams.
Nitrogen tetroxide taken	18·1482	19·2445	22·5910
Gain on passing nitric oxide..	0·1063	0·1500	0·3092
Corresponding to trioxide....	0·2693	0·3800	0·7833
Containing peroxide, NO_2....	0·1630	0·2300	0·4741
The total tetroxide is thus reduced to	17·9852	19·0145	22·1169

	I.	II.	III.
	parts.	parts.	parts.
Trioxide per 100 of tetroxide .	1·497	2·000	3·542

	I.	II.	III.
Freezing point of mixture....	−10·91°	−11·18°	−11·83°
Depression..................	0·77°	1·04°	1·69°
Depression for 1 part trioxide per 100 tetroxide..........	0·514°	0·520°	0·477°
Molecular weight of trioxide..	80·9	81·0	92·7

The calculated molecular weight of N_2O_3 is 76·0; hence the trioxide appears to show little, if any, tendency to form complex molecular groupings similar to those of P_4O_6, As_4O_6, and Sb_4O_6, with a percentage of from 1·5 to 2·0 per cent. in the solvent. Possibly the higher result, when 3·5 per cent. was present, may be due to polymerisation, but it is not a large error, when the difficulties of experiment are considered. It would have been desirable still further to increase the percentage of trioxide; but, if this is done, the difficulties of handling become very great, because the tendency of the trioxide to evaporate and decompose is greatly increased. Moreover, it is not easy at −20°, the temperature employed, to cause the trioxide to absorb more nitric oxide, except under pressure.

It may, therefore, be concluded, that, so far as these experiments go, the formula of the trioxide is really expressed by its name. Whether, on attaining a higher concentration, polymerisation would result cannot be easily decided; and it must be borne in mind that any large increase in percentage would bring into play other forces which, of themselves, produce abnormal results.

5. *Some of the Properties of the Trioxide.*—The trioxide does not solidify even at −90°. This was proved by saturating tetroxide with nitric oxide at −20° in a test-tube, and cooling the mixture by placing it in liquid nitrous oxide. A mass of crystals was obtained, apparently deep-blue, but it was possible, by means of a suitable rod, to squeeze out from them a blue liquid, leaving the crystals of a much paler colour. The mixture obviously consisted of colourless crystals of tetroxide, coloured blue by liquid trioxide. An attempt was made to force into this cooled mixture nitric oxide under a slight pressure, but more absorption did not appear to take place. It would be interesting to try whether liquid nitric oxide would effect any further change; but the experiment would be a difficult one.

The trioxide mixes with liquid nitrous oxide; for on pouring some of the blue liquid into about 30 c.c. of that liquid, complete mixture occurred. Some of the tetroxide solidified, and separated in white crystals; when the nitrous oxide had nearly evaporated away, the blue colour was no darker, and a blue, semi-solid mass remained, consisting, as usual, of a mixture of trioxide and tetroxide.

The conversion of tetroxide into trioxide may be effected at −99° by a current of nitric oxide, in presence of nitrous oxide, and, indeed, in its absence. The passage of the nitric oxide causes the nitrous oxide to evaporate so rapidly as to freeze; hence the lower temperature. We see, therefore, that the equation $N_2O_4 + 2NO = 2N_2O_3$ is realised even at this very low temperature.

The combination of tetroxide with nitric oxide takes place in preference to that with oxygen; and the combination of the trioxide with oxygen, if it takes place at all in the liquid state, is a very slow one. On passing a current of oxygen through tetroxide containing trioxide, the blue colour disappears very slowly, much oxygen escaping; and, indeed, I am of opinion that the apparent change is produced by removal of nitric oxide, rather than by its oxidation to tetroxide, for

12

any indifferent gas produces this change when passed through the blue liquid; moreover, the amount of substance is greatly lessened.

Richardson has observed (Trans., **51**, 397) that on heating one limb of a bent sealed tube containing nitric peroxide, the other limb being placed in a freezing mixture, the liquid condensing in the cold limb was dark-blue. It was tetroxide containing trioxide; and this in presence of oxygen sufficient to have restored it to its original condition of tetroxide had it been capable of combination. On warming the blue liquid, it became green, and finally red; the residue, therefore, must have been peroxide, and the mixed gases in the tube must have consisted of nitric oxide, oxygen, and gaseous peroxide. But on again cooling, a *blue* liquid condensed, showing that even when a mixture, theoretically capable of yielding peroxide, was cooled, combination had not gone beyond the stage of trioxide. Richardson remarks :—"It would appear that combination of nitric oxide with nitric peroxide takes place more readily than that of oxygen with nitric oxide or of oxygen with the trioxide, provided there is an excess of peroxide."

The solution of the mixture of tetroxide and trioxide in nitrous oxide did not appear to darken in colour on concentration. It occurred to me that, even at this low temperature, dissociation was taking place. The constantly escaping gas of the nitrous oxide appeared to be carrying with it some nitric oxide, for, on reaching the mouth of the tube, it had a faint red colour. To test this point, the mouth of the tube was loosely closed, and a tube from an oxygen bottle was introduced into the gas. After a considerable amount of the nitrous oxide had evaporated, more than sufficient to carry out any gas which might have been present in the tube, some oxygen was admitted. A red colour was at once produced in the tube, showing that the surmise was correct. Nitrogen trioxide appears, therefore, to dissociate at even so low a temperature as —90°.

A further experiment was made to test the solubility of nitric oxide in liquid nitrous oxide. A current of nitric oxide was passed through the liquid for about five minutes, and the nitrous oxide was then boiled so as to expel the gas from the tube. On adding some tetroxide, the liquid monoxide remained colourless, implying the non-solubility of nitric oxide. As the boiling point of nitric oxide is given as —150·6°, it is still much above its liquefying point.

The solution of nitrogen trioxide in nitrous oxide has a clear, deep-blue colour, like cobalt glass. It was examined with a spectroscope, and exhibits an absorption band between 544 and 590 λ, but is, as might be expected, totally devoid of the flutings of nitric peroxide; indeed, at that temperature, nitric peroxide does not exist, being wholly converted with its polymeride, nitrogen tetroxide.

XXXVIII.—*The Action of Light on Phosphorus and some of the Properties of Amorphous Phosphorus.*

By ALEXANDER PEDLER, F.I.C.

THAT ordinary phosphorus when exposed to the action of light under water for a considerable period becomes coated with a reddish and more or less opaque layer is a fact which has long been known. The first explanation which was given of the change was that a suboxide of phosphorus, P_4O, was formed, but when amorphous or red phosphorus was discovered, and its properties worked out by Schrötter, the explanation of this change of colour of phosphorus was simple, and it was then believed that no such compound as P_4O existed. Recently, however, it seems to have been proved by Reinitzer and Goldschmidt (*Ber.*, **13**, 848) that P_4O does exist, and its properties are described by them. Schrötter therefore appears to have been the first to prove the formation of red phosphorus from ordinary phosphorus by the action of light, and he also extended his observations to the action of heat on ordinary phosphorus, and showed that it had the same effect as light. Since this discovery, amorphous phosphorus has been prepared on a commercial scale by the action of heat on ordinary phosphorus, but even with all the improvements in manufacture, it does not seem possible to convert the whole of the ordinary phosphorus into the amorphous allotropic form, and such processes as treating the mixture of the two allotropic forms of phosphorus with carbon bisulphide, or of boiling it with solution of potassic or sodic hydrate have to be resorted to, in order to dissolve away the ordinary phosphorus from the amorphous phosphorus, the latter being unaffected by these reagents.

Red phosphorus is thus described by Schrötter ("Gmelin's Chemistry," 2, 109): "Amorphous phosphorus thus obtained (that is, by the action of heat or of light) is a soft powder destitute of crystalline structure, varying in colour between carmine and scarlet, sometimes even of a blackish-brown tint. When heated in a liquid, it becomes darker, and after some time acquires a deep violet colour. Amorphous phosphorus . . . by repeated distillation is converted into ordinary phosphorus . . . the change takes place at 260° C."

Another of the properties of amorphous phosphorus that may be noted is that it is easily dissolved by nitric acid, &c. But although the properties of amorphous phosphorus are thus described, the statements as to properties vary considerably in different text-books, original memoirs, &c.

It is well known that a third variety of phosphorus has been described as metallic or rhombohedral phosphorus. It was prepared by Hittorf by heating phosphorus with metallic lead to a temperature approaching redness for 10 hours, after which the metallic lead was dissolved out by dilute nitric acid, &c. The description of this kind of phosphorus is: "Metallic phosphorus is a brightly lustrous dark crystalline mass, which in thin plates possesses a red colour, and consists of microscopic rhombohedra . . . . it appears to conduct electricity better than the amorphous variety, and it requires to be heated to a temperature of 358° before it is converted into ordinary phosphorus. This variety is also formed when amorphous phosphorus is heated under pressure to a temperature of 580°" (Troost and Hautefeuille; Roscoe and Schorlemmer, "Treatise on Chemistry," 1, 472).

The following is then a very brief comparison of some of the distinctive properties of these three forms of phosphorus as generally given:—

Ordinary phosphorus.	Amorphous phosphorus.	Rhombohedral or metallic phosphorus.
Slightly yellow or almost colourless	From scarlet or red to almost violet colour	Yellow to deep red colour, metallic lustre.
Crystalline*	Amorphous	Crystalline (rhombohedral).
Soluble in carbon bisulphide	Insoluble in carbon disulphide	Insoluble in carbon bisulphide.
Soluble in sodic or potassic hydrate solution	Insoluble in sodic or potassic hydrate solution	Insoluble in sodic or potassic hydrate solution.
Easily oxidisable in air	Stable in air	Stable in air.
Melts at 44°. Boils at 290°	Reverts to ordinary phosphorus at 260°	Formed at high temperatures only, such as 580°, and re-forms ordinary phosphorus at 358°.

The following experiments form part of a considerable series which had been undertaken to test the effect of strong sunlight on a variety of substances. The experiments which will be described may be divided into several groups, the first of which will be experiments made in sunlight and at ordinary temperatures. It is needless to say that although single experiments are described in each case, the experiments have been repeated and confirmed. It will probably be only necessary to describe one of these experiments in detail to show the method of working and the results; the remaining experiments in this section will subsequently be briefly given in tabular form.

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* For forms of crystals see W. D. Hermann, *Ber.*, 6, 1415.

A clear, almost saturated solution of phosphorus in carbon bisulphide was sealed up in a glass tube, so that the tube was almost filled with the liquid. In the dark, the solution showed absolutely no change, and remained transparent. It was exposed to the direct light of a tropical sun at Calcutta on April 16, 1887, and within a few minutes a yellowish-red precipitate commenced to deposit on the sides of the tube, and the whole of the interior was soon covered.* The daily exposure to sunlight was continued till May the 4th, when the tube was opened. The solution still showed a considerable amount of unchanged phosphorus. The precipitated phosphorus was washed with carbon bisulphide, and with a mixture of carbon bisulphide and alcohol. A bright red powder was thus obtained, which, on microscopic examination, was found to consist of particles about half of which were of a bright sulphur-yellow colour, and the remainder of a bright red. This sample of allotropic phosphorus appeared to be fairly permanent in the air, and even after standing for several days in a hot moist atmosphere, it remained practically unchanged. The powder was also quite unaffected by such solvents as water, alcohol, ether, benzene, carbon tetrachloride, and carbon bisulphide.

On the other hand, however, the red powder was readily dissolved in a warm dilute solution of sodic hydrate with evolution of gaseous phosphuretted hydrogen, but the gas evolved was not spontaneously inflammable. Some of this allotropic phosphorus was tested in a fusing-point tube up to 305°, but it showed no tendency to revert to ordinary phosphorus, nor did it show any sign of change whatever. Heated cautiously in a bulb tube, a yellow sublimate was obtained, and the yellow sublimate was soluble in warm sodic hydrate solution. It was also partially soluble in carbon bisulphide, and this solution contained ordinary phosphorus. The yellow insoluble portion when heated in air burnt like ordinary phosphorus. In the bulb a bright red residue was left, which remained permanent at a rather high temperature, and which, on examination under the microscope, showed no yellow particles at all. The red particles were also less soluble in warm sodic hydrate solution than the original allotropic phosphorus.

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* A. Lallemand (*Compt. rend.*, **70**, 182; also *Watts's Dict. Chem.*, 2nd Suppl., 957), in describing a similar experiment, says that a solution of sulphur in carbon bisulphide is much more quickly changed into the allotropic variety of sulphur than the solution of phosphorus in carbon bisulphide is changed. The reverse to this has been found to be the case in a great number of experiments which have been made at Calcutta, and the solution of phosphorus in carbon bisulphide is much more sensitive to tropical sunlight than a solution of sulphur in carbon bisulphide.

Exposure to Strong Tropical Sunlight at Ordinary Temperatures.

A. *Solutions of Phosphorus in Liquids containing no Oxygen, or with no Oxygen present.*

Solution or condition of phosphorus.	Period of exposure.	Description of properties of allotropic phosphorus formed.
Solution of ordinary phosphorus in carbon bisulphide	18 days....	Bright red powder, consisting of red and yellow particles mixed; fairly permanent in air; insoluble in alcohol, ether, benzene, carbon tetrachloride, &c. Acted on by warm dilute solution of soda with evolution of phosphine (not-self-inflammable). Does not revert to ordinary phosphorus at 305°.
Solid phosphorus in Sprengel vacuum	27 days....	Brick-red powder, consisting of red and yellow particles, some being translucent, and allowing a sulphur-yellow and ruby-red light to pass through. Insoluble in usual reagents, soluble in warm soda solution with evolution of phosphine. Does not revert to ordinary phosphorus at 300°.
Solid phosphorus with a little iodine in Sprengel vacuum	21 days....	Brick-red powder, consisting of many translucent particles of sulphur-yellow and orange-red, and some of bright red colour. Easily attacked by warm dilute soda solution, phosphine coming off in abundance.
Solid phosphorus with iodine in Sprengel vacuum	2 months (May and June, hottest months of Indian year)	Dark-red powder, consisting principally of transparent and apparently crystalline, red particles, with a few transparent sulphur-yellow particles. Fairly easily soluble in hot solution of soda with evolution of phosphine.
Solution of phosphorus in carbon bisulphide with a little iodine	A few days.	At first bright yellow precipitate, gradually darkening, on lengthened exposure, to a bright red, many of the particles of which were transparent, and of red and yellow colour. Moderately easily soluble in hot solution of soda with evolution of phosphine.
Solution of phosphorus in carbon bisulphide with a small quantity of PBr_3	Some days..	After one hour's exposure, bright sulphur-yellow precipitate only: after two hours more, the precipitate had become orange, but the allotropic phosphorus did not further darken.
Solution of phosphorus in phosphorus trichloride	1 month....	Bright orange powder consisting of a large proportion of transparent, yellow particles, and of a few transparent, reddish particles. Slowly soluble in warm solution of soda with evolution of phosphine.
Solution of phosphorus in benzene	1 month....	Orange-coloured powder insoluble in carbon bisulphide, &c. Insoluble in sodic carbonate solution, but soluble in warm solution of soda with evolution of phosphine.
Solution of phosphorus in chloroform	1 month....	Bright yellowish-orange precipitate. In this case the particles appeared amorphous under the microscope, and no crystalline structure could be detected. Soluble in warm solution of soda with evolution of phosphine.

A. *Solutions of Phosphorus in Liquids containing no Oxygen, or with no Oxygen present—continued.*

Solution or condition of phosphorus.	Period of exposure.	Description of properties of allotropic phosphorus formed.
Solution of phosphorus in turpentine	1 month....	At first no allotropic phosphorus formed, but after a month a small quantity of yellow allotropic phosphorus was produced; this was easily soluble in warm solution of soda with evolution of phosphine.

The above experiments, it will be seen, were all made at the ordinary temperature of the air, and in strong direct sunlight, and the general result of these was, that a mixture of red and yellow coloured particles of phosphorus, many of them transparent and with a tendency to show crystalline structure, was obtained; this phosphorus was quite insoluble in carbon bisulphide, but soluble in hot dilute sodic hydrate solution with evolution of phosphuretted hydrogen.

An attempt was made to obtain only the yellow form by working with diffused daylight, and the following is a description of one of the experiments:—A small quantity of phosphorus bromide was mixed with a solution of phosphorus in carbon bisulphide, and placed in a sealed tube so that only a minute bubble of air was left at the top. The tube was exposed to strong diffused daylight, but so that the direct rays of the sun could not fall upon it, when a bright sulphur-yellow precipitate appeared. On standing a day or two under similar conditions, the colour of the precipitated phosphorus changed to orange. It was thought that the action was going on too rapidly and perhaps at too high a temperature, so the tube was immersed in a large cylinder filled with cold water. The separated phosphorus continued to darken in colour under the influence of light for some months, till it became a bright red. The precipitated phosphorus was purified in the ordinary way, and under the microscope it showed a mixture of transparent and perhaps partially crystalline particles, and also of amorphous particles. Many of the transparent particles were of a bright yellow colour, and of the amorphous some were bright yellow and others red. With dilute sodic hydrate solution, a small quantity of phosphuretted hydrogen was evolved in the cold, and, on boiling, the whole of the substance readily dissolved. Thus it would appear that the first form of phosphorus insoluble in carbon bisulphide is of a yellow colour, and that the more slowly the allotropic phosphorus is formed by the action of light, the more readily it is acted on by sodic hydrate solution. The experiment also appears to indicate that as the particles of allotropic phosphorus grow larger, they deepen in colour.

In the above experiments on the formation of allotropic phosphorus, it will be noticed that either solutions of phosphorus in liquids containing no oxygen have been used, or that the experiments have been made in such a way as to prevent the possibility of any oxygen combining with the phosphorus. In a few other cases, solutions of phosphorus in liquids containing oxygen have been used with the following results:—

Exposure to Strong Tropical Sunlight at Ordinary Temperatures.

B. *Solutions of Phosphorus in Liquids containing Oxygen.*

Solution or condition of phosphorus.	Period of exposure.	Description and properties of allotropic phosphorus (if any) formed.
Solution of phosphorus in mixture of carbon bisulphide and alcohol	2½ months..	Orange-scarlet powder containing a few bright yellow, transparent particles, the greater number being of a red-orange colour and somewhat opaque. Somewhat easily soluble in warm solution of soda with evolution of phosphine..
Solution of phosphorus in ether	1 month.....	Bright yellow powder, of which many particles were quite transparent. Insoluble in carbon bisulphide, easily soluble in hot dilute solution of soda with evolution of phosphine.
Solution of phosphorus in valeric acid	1 month....	No allotropic phosphorus formed, but an oily liquid was contained in the valeric acid in which phosphorus was present, probably in oxidised state.
Solution of phosphorus in amyl alcohol	1 month....	No allotropic phosphorus formed. Oxidised phosphorus appeared to be present in the amyl alcohol.

The general result of these experiments is, therefore, that solutions of ordinary phosphorus in liquids containing oxygen, on exposure to light, show a tendency for the phosphorus to combine with the liquid containing oxygen, and that allotropic phosphorus cannot be looked for with any certainty.

All the above experiments having been made at the ordinary temperature of the air, the production of allotropic phosphorus at higher temperatures was tried. The following are some of the results:—

Exposure to Tropical Sunlight at Higher Temperatures or to High Temperature alone.

Solution or condition of phosphorus.	Temperature, &c.	Description and properties of allotropic phosphorus formed.
Ordinary phosphorus in Sprengel vacuum	Phosphorus boiling *in vacuo* in sunlight	At first yellow sublimate, but colour rapidly darkening to red. The allotropic phosphorus consisted of bright, glistening, orange-red particles, most of them being quite transparent; some were sulphur-yellow, and others orange, and the particles appeared crystalline. Insoluble in carbon bisulphide. Very slowly acted on by boiling soda solution.
Ordinary phosphorus in Sprengel vacuum	Kept in the form of vapour in sunlight	In this experiment the sun's rays were concentrated on the phosphorus vapour by a large lens. Bright scarlet powder, containing no yellow particles, but only transparent orange-red and red particles like plates, which had a very distinct action on polarised light, the particles appearing distinctly crystalline. Very slowly acted on by hot soda solution.
Solution of phosphorus in carbon bisulphide with phosphorus tribromide added	100°	No allotropic phosphorus formed.
Ditto	200° to 210°.	Yellow allotropic phosphorus. Acted on by hot solution of soda with evolution of phosphine.
Solution of phosphorus in carbon bisulphide with a little iodine added	100°	Bright orange-red allotropic phosphorus, consisting of a mixture of yellow and orange-red particles. Slowly acted on by hot solution of soda.
Solution of phosphorus in carbon bisulphide	100°	No allotropic phosphorus.
Ditto	150°	Ditto
Ditto	200°	Ditto
Ditto	230°	Bright orange-red glistening powder, consisting of transparent particles of red to orange colour, and apparently of crystalline nature; also acting strongly on polarised light. Very slowly soluble in hot solution of soda with evolution of phosphine.

The general result of these experiments is, therefore, that the allotropic phosphorus obtained by the action of moderate heat only, or with the addition of light, from ordinary phosphorus is generally distinctly darker in colour than that obtained at low temperatures, and that it is also less easily acted on by dilute hot solution of sodic hydrate.

The properties of the allotropic phosphorus obtained in the above experiments have been carefully compared with the properties of many samples of commercial amorphous phosphorus, and with those of rhombohedral or metallic phosphorus, as obtained by Hittorf's process. In the course of these experiments it has been found that some of the properties of amorphous phosphorus, as described in text-books, are rather misleading. Some of these points are as follows:—

The term amorphous phosphorus itself appears to be misleading, and practically incorrect, and from the careful microscopic examination of eight samples of amorphous phosphorus, some obtained from England, and some from Germany, it has been shown that in all the samples examined the great bulk of the powder consists of transparent, ruby-red, more or less crystalline particles, which have a decided action on polarised light, indicating that most probably they are not amorphous. By careful elutriation, commercial amorphous phosphorus can be divided into a very fine powder, of very decided red colour, and into almost black, shining particles. The latter, under the microscope, are practically all transparent, giving a ruby-red light, and seem to be crystalline in nature, from their action on polarised light. In the finer powder the crystalline form is not so well marked, but many of the particles are transparent, allowing a ruby-red light to pass through, and they also act fairly strongly on polarised light. The red powder, when heated with dilute sodic hydrate solution, yields slight, but distinct, amounts of phosphuretted hydrogen, and the same powder, after having been much more finely powdered and treated with the *same* solution of sodic hydrate, yielded a larger amount of phosphuretted hydrogen. The dark, more or less crystalline particles yield no phosphuretted hydrogen on being boiled with a solution of sodic hydrate of the same strength as used in the last experiment, but after these coarser particles had been powdered extremely finely, and the very finely divided powder treated with the same solution as before, namely that with which the coarse powder had previously refused to give phosphuretted hydrogen, a rather large amount of phosphuretted hydrogen was evolved. At the same time the action of powdering the coarse particles was to render the almost black colour a distinct red-brown. The action of sodic hydrate solution on the so-called amorphous phosphorus, therefore, is evidently, to a certain extent, dependent on the state of division of the phosphorus though ordinary commercial amorphous phosphorus is supposed to be unacted on by sodic hydrate solution, as the latter is used as a method of purifying it from ordinary phosphorus. It might be said that ordinary phosphorus may have been present in the amorphous phosphorus, but this point was carefully enquired into, and absolutely no ordinary phosphorus could be detected. The methods used were solution by carbon bisulphide, and also heating the amorphous phosphorus in a vacuum to a moderate temperature for long periods, when ordinary phosphorus, if present, would have sublimed as in Hermann's experiments (*Ber.*, **6**, 1415).

Another property of amorphous phosphorus is said to be that at a temperature of 260°, it is converted, or begins to be converted, into ordinary phosphorus. The following experiments were made on this point:—Seven samples of commercial amorphous phosphorus, some from England and some obtained from Germany, and one sample of rhombohedral phosphorus, were heated at 305—310° for two hours. No signs of any change could be detected in the phosphorus. The same eight samples were heated in a bath of melting lead (temperature 326°), and no change could be detected. The same eight samples were heated in the vapour of boiling mercury for a short time (temperature 357·25°), and no change could be detected; but when heated in the vapour of boiling sulphur (temperature 445°), it was found that although the samples of phosphorus did not appear to undergo any reversion, yet a certain amount of vapour passed away from the surfaces, which vapour was oxidised on coming in contact with air. The boiling point of ordinary phosphorus is said to be 290°, so that the temperature of the bath in this instance was about 155° above the boiling point of ordinary phosphorus.

It will also have been noticed in the case of several of the samples of allotropic phosphorus made by the action of light, that these were unchanged by exposure to temperatures of about 305°.

Experiments of similar nature were made with the so-called amorphous phosphorus in vacuous tubes, so arranged that the phosphorus was heated while the upper part of the tube was kept cool. The phosphorus was kept at 100° for three or four days, when no change took place in the phosphorus, nor was any ordinary phosphorus sublimed. The phosphorus was then kept for two days at 200—210°, and again no change ensued. The amorphous phosphorus in a vacuum was next exposed to the vapour of boiling sulphuric acid (temperature 327°) for between four and five hours, and no change took place in the phosphorus, nor was any ordinary phosphorus sublimed. Next the amorphous phosphorus was heated in a bath of the vapour of boiling mercury (357·25°) for two hours and a quarter, when a *very* small amount of ordinary phosphorus was sublimed, but the amount so produced was not more than about one-twentieth of the amount used. A temperature of 445° was also used by a bath of boiling sulphur for a period of three hours, and under these circumstances about one-fifth of the amorphous phosphorus underwent change, and sublimed as ordinary phosphorus into the cool part of the tube. It may, therefore, be concluded that either in a vacuum, or at the ordinary pressure, there is no change whatever of amorphous into ordinary phosphorus at 260° as ordinarily stated, and that there is no practical change up to temperatures of nearly 358°, after which in a vacuum a feeble change commences, by which the vapour of ordinary phosphorus is evolved, but this change, even up to 445°, is exceedingly slow.

It may also be remarked that the behaviour of metallic or rhombohedral phosphorus is exactly similar to that of amorphous phosphorus under these circumstances, for the temperature at which rhombohedral phosphorus begins to change is stated to be 358°.

Amorphous phosphorus is also generally stated to be quite permanent in the air. Thus Roscoe and Schorlemmer say ("Treatise on Chemistry," 1, 470), "This substance (red phosphorus) can be exposed to the air for years without undergoing any alteration." It is, however, known that some samples of amorphous phosphorus become damp on exposure to air, and Groves (*Pharm. J. Trans.* [2], 6, 643; and *Watts's Dict. Chem.*, Suppl., 934) has shown that the oxidation may sometimes go on to a considerable extent. In text-books, however, the oxidation of amorphous phosphorus is referred to the presence of ordinary phosphorus, and thus Roscoe and Schorlemmer again say (p. 471), "All the commercial amorphous phosphorus, however, contains traces of the white modification, and this undergoes oxidation in the air, so that the mass always has an acid reaction, owing to the formation of phosphorous and phosphoric acids." In a very hot and very moist climate, like that of Calcutta, where all these experiments have been made, the rapid change or oxidation of commercial amorphous phosphorus is a very familiar phenomenon. The experiment has been tried with the same sample of phosphorus four times in succession, by allowing the sample to oxidise, then removing the oxidised products by careful washing, then drying, and on standing, oxidation has recommenced as stated above on four successive occasions. This in itself is probably a sufficient proof that the cause of the oxidation is not to be found in the small quantity of ordinary phosphorus which might have been present in the amorphous phosphorus as at first manufactured, for the successive oxidation would require a fresh existence of ordinary phosphorus in each case. In order to set the question at rest, samples of very carefully purified amorphous phosphorus have been taken, in which no trace of ordinary phosphorus could be detected, and which had been allowed to oxidise once, and the oxidised products removed, and yet when exposed to the moist climate of Calcutta in loosely corked tubes, they have become moist, and decidedly acid in reaction within the short space of six days only.

To show the extent to which such oxidation may proceed, two samples of commercial amorphous phosphorus, practically free from any ordinary phosphorus, were allowed to oxidise in very loosely-stoppered bottles for about three years. At the end of this period the amount of oxidised phosphorus was determined. In the first case, of the original weight of 55·3 grams of amorphous phosphorus, 9·3 grams had oxidised, or 17·1 per cent. of the original amount; and in the second case, 63·8 grams of amorphous phosphorus had yielded 9·8 grams of oxidised phosphorus, equalling 15·4 per cent. of the original weight. The acid liquids in both cases only contained phosphorus and phosphoric acids, and no hypophosphorus or hypophosphoric acids could be detected. The relative amounts of phosphorous acid and of phosphoric acid in the acid liquids formed on oxidation of amorphous phosphorus do not appear to be fixed, and they were as nearly as possible 10 parts of phosphorous to 43 parts of phosphoric acid in the first case, and 10 parts of phosphorous to 75 parts of phosphoric acid in the second case.

It has been noticed in these and similar cases of oxidation of amorphous phosphorus, that the oxidation appears to go on steadily, notwithstanding that the amorphous phosphorus is covered over with the solution of the two acids, and, therefore, presumably kept from actual contact with the oxygen of the air. To test whether this is the case, and whether the amorphous phosphorus really does continue to change under these circumstances, the following experiments have been made:—

Experiment 1. Some commercial amorphous phosphorus which had been exposed to the air for more than two years, and which had thus undergone a large amount of oxidation, during which any ordinary phosphorus which may originally have been present must have been oxidised, was very carefully purified by washing with water till free from all acidity, and then dried. 1·4290 grams of this pure, dry red phosphorus were digested in a flask loosely covered with a watch-glass, at a temperature of about 60°, with a rather concentrated solution of orthophosphoric acid. The digestion was allowed to go on for 12 days, and throughout the whole period a strong odour of phosphoretted hydrogen was evolved. After the 12 days' digestion, the red phosphorus was washed and weighed, and found to be only 1·3913 grams. There had thus been a loss of 2·64 per cent. of the original weight. The phosphoric acid solution was found to contain distinct amounts of phosphorous acid, but no hydrophosphorous acid. The following reaction would indicate how phosphorus can act on phosphoric acid with the production of phosphorous acid and phosphoretted hydrogen:—$3H_3PO_4 + 6H_2O + P_4 = 6H_3PO_3 + PH_3$.

Experiment 2. To further test this action, and to prove that the loss in weight of the red phosphorus did not depend on any oxidation due to the presence of air in the reaction, some of the purified red phosphorus was sealed up in a tube with a known quantity of a rather dilute solution of orthophosphoric acid. 100 c.c. of the original phosphoric acid which contained 1·1796 grams of P_2O_5, after digestion with the pure red phosphorus at 100° for seven days, contained an amount of phosphorus equal to 1·1916 grams of P_2O_5, and the solution also contained distinct amounts of phosphorous acid. There had thus been, even in the absence of air, a distinct action of red phosphorus on dilute solution of phosphoric acid, and an increase equal to about 1 per cent. had taken place in the weight of the P_2O_5 present. It is clear then that red phosphorus can reduce phosphoric to phosphorous acid, and, as the latter can itself oxidise to phosphoric acid, it is possible that in the oxidation of red phosphorus, in the cases above alluded to, oxidation and deoxidation go on continually, or, if such a simile or analogy may be used, then the oxidation of red phosphorus in the air may be compared with the oxidation of iron in the air.

Experiment 3. It was thought desirable to test whether ordinary phosphorus had a similar power of reducing phosphoric acid, and pieces of clean ordinary phosphorus were placed in sealed tubes with dilute solutions of phosphoric acid of known strength. Two experiments were started, one in which the tube containing the phosphorus was heated at 100° for seven days, and in which case the small surface of the melted phosphorus only was exposed to the action of the liquid, while in the second case the action was allowed to go on for eight days at about 30° to 35°, the phosphorus being first melted, and then the tube violently agitated, until the phosphorus solidified in very minute globules, thus exposing a very large surface to the action of the phosphoric acid. In both cases the phosphoric acid used contained 1·1796 grams P_2O_5 in 100 c.c. In the first case, after the action of the small surface of ordinary phosphorus on the dilute phosphoric acid for seven days at 100°, the liquid contained in 100 c.c. 1·1820 grams P_2O_5, showing that in this case the action was extremely feeble, while, further, no distinct trace of phosphorous acid could be detected in the liquid. In the case where the action took place with the ordinary phosphorus in a finely-divided state for eight days, 100 c.c. of the liquid contained 1·2148 grams of P_2O_5, showing that in this case there had been very decided action. The solution also was found to contain distinct amounts of phosphorous acid.

Experiment 4. Some of the purified commercial amorphous phosphorus used in the previous experiments was also digested in distilled water at about 60°, and although the digestion was continued for a week, during the whole period a decided smell of phosphoretted hydrogen was evolved, and, at the end of the time, the watery solution contained distinct amounts of the acids of phosphorus, and gave a considerable precipitate with the molybdate test. The watery solution, after the week's digestion, yielded no less than 0·0148 gram of $Mg_2P_2O_7$, equivalent to 0·00413 gram of phosphorus. The weight of the purified red phosphorus used in the experiment was 0·7924 gram, and thus 0·52 per cent. of the phosphorus had been acted on, and passed into solution.

Experiment 5. As in the last experiment, also, it might be objected that the oxidation was due to the fact of the experiment being made in the air, 0·5638 gram of purified red phosphorus was digested at 100° in a sealed tube with 25 c.c. of water for six days. The weight of the red phosphorus was then found to be 0·5599 gram, and there had, therefore, been a loss of 0·69 per cent. The watery solution also contained oxidised phosphorus, and, with the molybdate test, a very distinct precipitate was obtained.

These experiments, therefore, would tend to show that so far from the so-called amorphous phosphorus being the inert and stable substance it is usually supposed to be, on the contrary, it is rather prone to change; it easily oxidises, and, also, it has a distinct power of deoxidising such compounds as phosphoric acid, &c.

In the foregoing descriptions, the properties of the allotropic phosphorus produced by the action of light only, that produced at moderate temperatures, and the commercial form of amorphous phosphorus, which is made at decidedly high temperatures, have been compared with one another. Specimens of rhombohedral or metallic phosphorus have also been prepared, and their properties compared with those of the other forms. The metallic phosphorus used has been prepared by two processes: first, that of dissolving ordinary phosphorus in lead at high temperatures, as described by Hittorf, and the second process, which appears to answer equally well, or perhaps rather better, by projecting dry commercial amorphous phosphorus in small quantities at a time into melted lead, kept at a rather high temperature, the lead being subsequently removed, and the metallic phosphorus extracted in the manner recommended by Hittorf. The general properties of this form of phosphorus, as described by Hittorf, are given in "Watts's Dictionary of Chemistry," 2nd Suppl., p. 993. It is unalterable in the air, and the crystals formed on the surface of the lead "are very thin, mostly bent, and transversely striated, whereby they acquire the aspect of rows of prismatic crystals; they are yellowish-red by transmitted light. The crystals enclosed in the mass of lead . . . . have a black-violet colour, and appear under the microscopic as rhombohedrons, nearly approaching the cube," &c. The specimens of metallic or rhombohedral phosphorus prepared in these ways, when examined under the microscope, showed that most of the particles were rather darker than those of ordinary commercial amorphous phosphorus, but some of the particles were also of a light colour. The fact that many of the particles of rhombohedral phosphorus are rather dark, may be almost expected when it is considered that they are crystallised from metallic lead, and when it is known that traces of metals will confer a dark colour on ordinary phosphorus (Blondlot, *Compt. rend.*, **70**, 856). The particles of metallic phosphorus are acted on by polarised light in a manner precisely similar to the forms of phosphorus produced from the ordinary variety, either by the action of light or heat, and to the ordinary commercial amorphous phosphorus. When the crystals of rhombohedral phosphorus, after careful purification from ordinary phosphorus, are heated with dilute sodic hydrate solution, extremely small quantities of phosphuretted hydrogen are given off. It was, however, also found that the same sample, after having been extremely finely divided by powdering, when heated with the same strength of sodic hydrate solution, yielded somewhat larger amounts of phosphuretted hydrogen; but still the quantity was very small.

It will thus be seen that in colour these crystals of rhombohedral phosphorus vary in a manner somewhat similar to that found in the case of the ordinary red phosphorus. Under the action of heat, metallic phosphorus also behaves in a manner practically similar to allotropic phosphorus. Sodic hydrate solution also acts on the varieties in a somewhat similar manner, the extent of the action apparently being dependent greatly on the state of division of the allotropic phosphorus; the very finely-divided particles of phosphorus obtained by the slow action of light, being vigorously acted on, and the larger and denser particles, obtained by the action of heat, being much less vigorously acted on. Similarly, also, the colour of the allotropic phosphorus seems to be, to a great extent, dependent on the size of the particles, for whilst in small particles, or when in thin layers, the allotropic phosphorus produced is yellow, the particles, on increasing in size, pass apparently through the shades of orange to red, and finally to a very dark colour.

No sample of so-called amorphous phosphorus, prepared in the various ways, as stated previously, has possessed wholly the properties of a true amorphous body, but all the methods of preparation, whether by the action of heat or light, yield a substance which is more or less transparent, and perhaps crystalline in its nature. So, also, all the numerous samples of commercial amorphous phosphorus examined appear to be distinctly of a crystalline nature. It might be said that the definite crystalline form of phosphorus in this condition should be capable of being determined, but phosphorus generally, in respect to crystallisation, appears to be an abnormal body, as was found by Hermann (*Ber.*, **4**, 1415). It would, therefore, appear that the term amorphous phosphorus, applied to the substance, is a distinct misnomer, and, so far from commercial amorphous phosphorus constituting a separate allotropic modification of this element, the conclusion arrived at from the work detailed in this paper is that the so-called amorphous phosphorus is really the same as the allotropic form called rhombohedral or metallic phosphorus, the very slight differences in character noticed between the substances in question being explained by the difference in the state of division and the slight differences in property due to their mode of formation. Whether the term amorphous phosphorus, also, can be truly applied to the forms of allotropic phosphorus, made by the action of light, is open to grave doubt; for, even in these cases, there appear to be distinct evidences of crystalline form, though it is true that a form of phosphorus which appeared to be amorphous was obtained in some of the experiments. Practically, however, it is believed it would be better to altogether discard the use of the term "amorphous" phosphorus.

XXXIX.—*The Action of Chlorine on Water in the Light, and the Action of Light on Certain Chlorine Acids.*

By ALEXANDER PEDLER, F.I.C.

THAT a solution of chlorine in water when exposed to the action of light gradually changes in composition is, perhaps, one of the best known facts in chemistry. The explanation of the change, as given in most modern text-books on chemistry, is that oxygen is evolved by the direct action of the chlorine with the formation of hydrogen chloride, according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$. The statement is also made that when chlorine-water is placed in direct sunlight, the *whole* of the free chlorine may thus combine with the hydrogen of the water, evolving its equivalent volume of oxygen. A proposal has indeed been made (Wolters, *Pogg.*, **94**, 579; *Ann. Chem. Pharm.*, Suppl., **4**, 63) to employ this reaction in measuring the chemical action of light. In direct tropical sunlight the decomposition of chlorine-water is so rapid that it can be used as a lecture experiment, and a strong solution of chlorine in water in the full blaze of the sun in the hot season in Calcutta, is actually seen to effervesce very decidedly. It is also stated in connection with this decomposition that "the rate of the decomposition of the water (by the chlorine) is influenced by the quantity of hydrogen chloride which has previously been formed, and the presence of this substance is said to greatly retard the action, according to a complicated law" (Roscoe and Schorlemmer, "Treatise of Chemistry," **1**, 124).

Berthelot (*Ann. Chim. Phys.* [5], **22**, 459) has, however, shown that the solubility of chlorine in water varies for the same temperature with the time of contact and the intensity of light, the variations being due to a slow decomposition of water with the formation of oxy-acids of chlorine, thus indicating that the equation given above, in some cases, at all events, is not strictly true.

Popper (*Annalen*, **227**, 161; also Abstr., 1883, **48**, 631) has subsequently made experiments proving that chlorine-water, on exposure to sunlight, is probably converted into hydrogen chloride and chloric acid, whilst oxygen is given off; perchloric acid is not formed, and the question as to the formation of hypochlorous acid was left unsettled. In a subsequent paper, the same author (*Annalen*, **231**, 137; also Abstr., 1886, **50**, 301), describing his further work on the subject, gives the following equation as representing the decomposition of chlorine-water by sunlight:—

$$5Cl_2 + 5H_2O = HClO_3 + 9HCl + O_2.$$

In the course of a long series of experiments made on the action of light on various substances and on different chemical reactions, certain facts have been discovered which prove that neither of the statements made above really represents the whole facts of the case, and that neither equation is wholly right, or wholly wrong.

The action, indeed, of chlorine on water, in the first place, requires certain conditions before it will take place at all; and secondly, it has been found that more than one action is possible when the conditions of exposure of light vary.

In the first experiments which will be described, the following was the plan of procedure. Pure moist chlorine was passed through glass tubes of known capacity, provided either with stopcocks at each end, or which could be easily hermetically sealed, until all the air was swept out; when this was effected, definite volumes of distilled water were run into the tubes, displacing the corresponding volume of chlorine, and the tubes were then sealed or the stopcocks closed, and the tubes exposed to the direct rays of the sun for certain periods. At the conclusion of the exposure, the tubes were opened, first under water, and any water which entered was measured, so as to note the contraction; next, the amount of any free chlorine left was estimated; and third, the volume of the oxygen produced was measured. It will be noticed that in the first equation given above, for every ten volumes of chlorine which act on the water, five volumes of oxygen should appear, and by Popper's equation ten volumes of chlorine would only yield two volumes of oxygen.

Experiment 1.—83·5 c.c. of chlorine were taken with 4 c.c. of water in a tube. As for both the equations, 1 mol. of chlorine requires 1 mol. of water, the quantities here used represent roughly 64 mols. of water to 1 mol. of chlorine. The tube was exposed for a month to strong diffused daylight, and for another month to the direct action of tropical sunlight in Calcutta, where all these experiments were made. The tube throughout remained strongly coloured, from the presence of free chlorine, and no change whatever in the intensity of the colour could be detected. On opening, it was found that no appreciable change had taken place; there was no diminution in volume of the gases in the tube, and it was still practically filled with chlorine.

Experiment 2.—A sealed tube, containing 47·5 c.c. of chlorine and 3 c.c. of water, giving roughly 88 mols. of water for 1 mol. of chlorine, was exposed to direct sunlight from January 29th, 1890, to February 11th, 1890. During the experiment the amount of sunshine was estimated by a Jordan's sunshine recorder, and there were 132 hours of bright sunshine out of a possible amount of 156·3 hours during this period. No perceptible diminution in the intensity of the colour of the chlorine could be detected throughout the exposure. On opening, 33·5 c.c. of chlorine out of the original 47·5 c.c. of chlorine were found to be unacted on, or that only 14·0 c.c., or 29 per cent. of the original amount of the chlorine, had acted on the water, while only 6·5 c.c. of oxygen had been formed, theory, according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$, requiring 7 c.c. of oxygen to be produced. So there must clearly have been a *very small* portion of the chlorine undergoing another reaction, possibly that suggested by Popper, that is, $5H_2O + 5Cl_2 = HClO_3 + 9HCl + O_2$, or some reaction similar to this.

Experiment 3.—51 c.c. of chlorine and 5 c.c. of water were exposed in a sealed tube to direct tropical sunlight for 14 days, during which there were, by the sunshine recorder, 137·1 hours of bright sunshine out of the possible amount of 165·3 hours. The above quantities represent a little more than 130 mols. of water to 1 mol. of chlorine. A slight diminution in the intensity of the colour of the chlorine could be detected during the experiment, but even after the 14 days, the colour of the chlorine was very strongly marked. On opening the tube, 27·6 c.c. of chlorine were still unacted on, and 11 c.c. of oxygen had been formed; 23·4 c.c. of chlorine, or about 46 per cent. of the original volume, had thus acted on the water, but instead of 11·7 c.c. of oxygen being produced, as is required by the equation $2H_2O + 2Cl_2 = O_2 + 4HCl$, only 11 c.c. were produced. Again, therefore, a *very small* amount of the oxygen had disappeared in the formation of one of the oxidised acids of chlorine.

Experiment 4.—79·5 c.c. of chlorine and 8 c.c. of water, representing roughly about 1 mol. of chlorine to nearly 140 mols. of water, were exposed to tropical sunlight from January 20th, 1890, to February 3rd, 1890, during which period there were 137·1 hours of bright sunshine out of the possible amount of 165·3 hours. Again, during the exposure the intensity of the colour of the chlorine scarcely changed, and at the close the tube had still a deep colour. On opening, 56·4 c.c. of free chlorine were found to be present, and there were only 6·2 c.c. of oxygen formed. Thus in this case only 23·1 c.c. of chlorine, or 29 per cent. of the gas originally present, had acted on the water, and instead of the formation of 11·5 c.c. of oxygen required by the equation $2H_2O + 2Cl_2 = 4HCl + O_2$, only 6·2 c.c. of oxygen were formed. There had in this case, therefore, been considerable combination of the oxygen to form an oxidised acid of chlorine.

Experiment 5.—37 c.c. of chlorine, and 10 c.c. of water, representing about 1 mol. of chlorine to 412 mols. of water, were exposed to tropical sunlight for 14 days, during which there were 137·1 hours of bright sunshine, as indicated by the sunshine recorder, out of the possible amount of 165·3 hours. Even after two days, there was a perceptible diminution in the intensity of the colour of the chlorine, showing that action was taking place, but the diminution of colour subsequently continued extremely slowly (if at all), and even after the 14 days, there was a distinct amount of free chlorine in the tube, as indicated by the colour. On opening it, 8·5 c.c. of free chlorine only were found, and there were 10 c.c. of oxygen formed. Thus, 28·5 c.c. of chlorine, or about 78 per cent. of the total amount used, had acted on the water, and instead of the 14·25 c.c. of oxygen which should have been formed according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$, only 10 c.c. of oxygen were formed, proving, again, that a certain amount of the oxygen had been utilised in forming one of the oxidised acids of chlorine.

The principal facts detailed in the above five experiments are summarised in the table (p. 617).

The general result of these experiments, therefore, is to show that chlorine and water, when placed in very strong tropical sunlight, have comparatively little action on each other, even when the number of molecules of water is as much as a hundred times as great as that required by theory; the action is larger, ranging up to, perhaps, nearly 50 per cent. of the possible amount, when the number of molecules of water is about 150 for every molecule of chlorine. When the number of molecules of water is more than 400 for every single molecule of

No. of Expt.	Vol. of Cl taken.	Vol. of H_2O used.	No. of molecules of H_2O for every 1 molecule of Cl.	Period of exposure to sunlight.	Percentage of Cl which had acted on the H_2O.	Vol. of O liberated for every 2 vols. of Cl which had disappeared.
1	83·4 c.c.	4 c.c.	64	2 months	No perceptible action	
2	47·5 ,,	3 ,,	88	132 hours*	29	0·93
3	51·0 ,,	5 ,,	130	137·1 ,,	46	0·94
4	79·5 ,,	8 ,,	140	137·1 ,,	29	0·54
5	37·0 ,,	10 ,,	412	137·1 ,,	78	0·70

chlorine, the reaction becomes much more rapid, but even then reaction only proceeds to the extent of about four-fifths of the possible amount.

Further, it would appear that with the smaller ratios of water and chlorine, the reaction becomes nearly that required by the equation $2H_2O + 2Cl_2 = 4HCl + O_2$, but that as the amount of water is increased, a certain amount of oxidised chlorine acids is formed, and that in addition to the simple action usually represented to occur, other actions represented by some such equation as that suggested by Popper ($5H_2O + 5Cl_2 = 9HCl + HClO_3 + O_2$) may take place.

In the case of ordinary chlorine water, supposing the water to be saturated, say, at 30° to 32°, which is about the average working temperature in a laboratory at Calcutta, the weight of chlorine in 100 c.c. of water would be about 0·5566 gram. In other words, the ratio of chlorine to water in such a sample would be 1 mol. of chlorine to about 708 mols. of water, and hence the results of the above experiments would show that with ordinary chlorine water the decomposition may be expected to be both more rapid and more complete than in the above cases, and that also the reaction may perhaps yield oxidised chlorine acids, and hence the quantity of oxygen evolved in the reaction will be comparatively small.

A very large series of experiments on the action of light on chlorine water has been made, and in these experiments three degrees of intensity of light were used. In some experiments the direct rays of the tropical sun in the hottest season of the Indian year were allowed to fall on the chlorine-water; in others, the experiments were carried on in very strong diffused daylight, by putting the apparatus in an open verandah facing the south, but so that the direct rays of the sun could not reach the apparatus; and, third, the experiments were made opposite the window, in a room with a north light only, so that only

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* Actual hours of full tropical sunlight as indicated by sunshine recorder.

Chlorine Water Exposed to full Tropical Sunlight.

No. of Expt.	Before exposure.	Period of exposure to sun-light.	After exposure to light.				Remarks.
	Amount of free chlorine in 10 c.c. chlorine-water.		Whether oxygen evolved.	Total amount of free acid found, calculated to equivalent weight of chlorine.	Amount of chlorine as hydrochloric acid.	Amount of chlorine as chloric acid determined by reduction with Zn-Cu couple, &c.	
1	gram 0·0305	10 days	large quantity	gram 0·0300	gram 0·0313	trace only	Solution colourless, no smell, no bleaching power in cold, but faint bleaching action when boiled with strong hydrochloric acid.
2	0·0296	several days	do.	0·0288	0·0301	„	Do. do.
3	0·0304	do.	do.	0·0292	0·0296	„	No bleaching action in cold, faint bleaching action on boiling with strong acids.
4	0·0299	do.	do.	0·0295	0·0284	—	Solution had distinct odour of hypochlorous acid, and very feeble bleaching action in cold.
5	0·0296	do.	do.	0·0288	0·0294	trace only	Solution colourless, no odour of chlorine or hypochlorous acid, no bleaching action in cold, but feeble bleaching action when heated with strong acid.
6	0·0372	17 days*	do.	0·0356	0·0348	0·0024 gram	Solution colourless, no odour, no bleaching action in cold, slight bleaching action on heating with acid.
7	0·0372	18 days†	do.	0·0338	0·0341	0·0031 „	Solution quite colourless, no free chlorine, but exceedingly faint smell of hypochlorous acid, no practical bleaching action in cold, but distinct bleaching action on heating with acid.

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* In the 17 days (in May, 1889) there were 148·5 hours of bright sunshine (by the sunshine recorder) out of a possible 236·8 hours.
† „ 18 „ „ „ 157·0 „ „ „ „ „ „ 250·1 „

Chlorine Water in Strong Diffused Daylight.

No. of Expt.	Before exposure.	Period of exposure to diffused daylight.	After exposure.					Remarks.
	Amount of free chlorine in 10 c.c. of solution.		Whether oxygen evolved or not.	Total amount of free acid found, calculated to equivalent weight of chlorine.	Amount of chlorine as hydrogen chloride.	Amount of chlorine as hypochlorous acid.	Amount of chlorine as chloric acid (by reduction with Zn-Cu couple, &c.).	
1	gram 0·0358	25 days	moderate amounts	gram 0·0320	gram 0·0320	none	gram 0·0038	Solution colourless, no odour, no bleaching action in cold, but slight bleaching action on boiling with hydrochloric acid.
2	0·0369	23 days	do.	0·0355	0·0337	none detected	0·0032	Solution colourless, faint odour, very slight bleaching power in cold, no chlorous acid.
3	0·0149	14 days	exceedingly small amounts	0·0146	0·0149 gram		none detected	Solution entirely colourless, no free chlorine detected, solution made alkaline bleached rapidly, no chlorous acid.
4	0·0139	14 days	scarcely any	0·0128	0·0135 „		0·0004 (traces only)	Solution colourless, smell of hypochlorous acid, gave strong reaction for hypochlorous acid by forming soluble salt with mercury,* no chlorous acid present, no hydroxyl present.

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* This reaction is used by Wolters (*J. pr. Chem.*, 7, 468) in detecting hypochlorous acid in presence of chlorine and other chlorine acids, and he has shown that the reaction can also be used for the quantitative estimation of hypochlorous acid.

feeble diffused daylight could act on the solutions. The usual method of experimenting was to place the chlorine water of known composition in flasks holding half a litre and upwards, almost filled with the liquid, and provided with tightly fitting corks and delivery tubes, the latter being placed under graduated tubes filled with water, and standing in pneumatic troughs. After exposure, the gas evolved was measured, and the contents of the flasks analysed. In the first set of experiments the effect of full tropical sunlight on chlorine water was determined, and the results are given in the table (p. 618).

In all these cases the volumes of oxygen evolved were determined, but in each experiment the gas collected fell considerably short of the theoretical amount. In the first place as shown above, small amounts of chloric acid were produced which would account for a diminution in the oxygen, and secondly, the oxygen evolved would probably first thoroughly saturate the liquid with the gas, and it was noticed in each case that on agitation of the liquid at the end of each experiment considerable effervescence took place. Thus the amounts of oxygen collected could not be used to indicate definitely the reaction which was going on.

The general result of the experiments with chlorine water exposed to direct tropical sunlight may, therefore, be said to be in favour of the simple equation $2H_2O + 2Cl_2 = 4HCl + O_2$ as representing practically the reaction, for the amount of chloric acid formed in each case was exceedingly small.

Next, the influence of strong diffused daylight as obtained in an open south verandah was tried on chlorine water, the experiments being so arranged that no direct rays of the sun could fall on the apparatus, while it could receive the strongest diffused light possible. The general results of these experiments are contained in the table (p. 619).

In order to further prove the existence of the hypochlorous acid in the last two cases, some of the solutions were divided into equal volumes, and one half neutralised with potassic hydrate, then mixed with the second half, and carefully distilled. In the distillate, considerable amounts of hypochlorous acid could be detected by the usual methods.*

It will be noticed in the case of these experiments in diffused daylight, that there were slight variations of the results, and that either hypochlorous acid or chloric acid, or both, were produced. The only variations in the circumstances of the experiments which could cause these differences were the possible variation in the intensity of the diffused light causing the reaction and the duration of the exposure. To test whether this was the cause of the variation in the results, some experiments were made inside a room, the apparatus being placed opposite a window with a north light, when only very moderate, diffused light could reach the chlorine water.

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* It may be desirable here to remark that considerable discussion has taken place between Göpner and Hugo Schiff as to the constitution of the so-called chlorine hydrate ($Cl_2,10H_2O$), the former considering this compound to be $HOCl, HCl, 9H_2O$, while the latter disputes this explanation of its constitution.

Experiment 1.—A sample of chlorine water, of which 10 c.c. contained 0·0195 gram of chlorine, was exposed to the action of the light from a north window for 37 days, and during the action, not a single bubble of oxygen gas escaped from the apparatus. At the end of the time, the liquid had a very faint yellow colour only, and had a smell of hypochlorous acid. With mercury, it gave a very decided reaction for the presence of hypochlorous acid, and the amount of this acid, as determined by this reaction, was 0·0089 gram in 10 c.c. The amount of chlorine in the hypochlorous acid as indicated by the liberation of iodine equalled 0·0077 gram.

Experiment 2.—In another experiment, chlorine water again yielded no gas after exposure for 38 days to the light from a north window, after which period the solution had become colourless, and it smelt strongly of hypochlorous acid. This acid was also proved to be present in considerable quantity by the reaction with mercury, &c. Chloric acid was also shown to be present in small amount in the exposed liquid.

Experiment 3.—In another experiment, an amount of chlorine water which, according to the equation $2H_2O + 2Cl_2 = 4HCl + O_2$, should have yielded about 74 c.c. of oxygen was exposed for 46 days in diffused daylight opposite the north window in a room, when only 5 c.c. of oxygen were evolved. The liquid became almost colourless, and was found to contain moderate amounts of hypochlorous and chloric acids, but no chlorous acid or hydrogen dioxide.

The most probable explanation of the general result of the above experiments on the action of strong and also more feeble diffused light appears to be that the first action of chlorine on water is to form hypochlorous acid and hydrochloric acid, according to the equation $H_2O + Cl_2 = HCl + HClO$, and that by the continued action of light, the hypochlorous acid itself changes into chloric acid.

That this is the most probable reaction is supported by such experiments as these. Chlorine water which contained 0·0355 gram of chlorine in 10 c.c., after standing for about 24 to 36 hours in rather feeble light, when tested by the usual mercury process of estimating hypochlorous acid, yielded in the same volume 0·0116 gram of this acid. After exposure to strong diffused daylight for 5 days, the amount was reduced to 0·0013 gram in 10 c.c. After 10 days' exposure, the acid could still be detected by the mercury process, but the amount was very small, and after 32 days no hypochlorous acid could be detected, and the liquid had practically ceased to bleach in the cold. At the conclusion, by the zinc-copper couple process, the amount of chlorine as chloric acid in 10 c.c. of this liquid was found to equal 0·0030 gram, or to about a tenth of the original weight of the chlorine in the chlorine water.

The problem can also be approached by the study of the properties of dilute solutions of hypochlorous acid. The usual statement as to this acid is, that only dilute solutions are stable, and that concentrated solutions are readily decomposed by exposure to sunlight, partly yielding chlorine and oxygen, while another part undergoes oxidation, yielding chloric acid. In all the cases dealt with in the previous experiments, very dilute solutions of hypochlorous acid would be present. It was therefore thought desirable to make some experiments on the action of diffused light on dilute hypochlorous acid, and the following are some of the results.

Experiment 1.—A sample of hypochlorous acid was obtained by the action of chlorine on mercuric oxide suspended in water. It was then allowed to stand over mercuric oxide and distilled; no free chlorine was given off during the distillation. The liquid was very feebly acid, and a few drops of potassic hydrate solution made it alkaline, but the alkaline solution as well as the original solution bleached vigorously. Both by the mercury test ($2Hg + 2HClO = HgCl_2HgO + H_2O$), and as judged by the action with potassic iodide and titration of the iodine by sodic thiosulphate, 10 c.c. of distilled liquid contained an amount of chlorine in the acid equal to 0·0316 gram of chlorine. 10 c.c. of liquid were also reduced by the zinc-copper couple, and found to contain hypochlorous acid equivalent to 0·0306 gram of chlorine. Exposed to the action of strong diffused daylight, after 10 days, 60 c.c. yielded 9 c.c. of gas, and on continuing the exposure for 10 to 11 days, a total of 18 c.c. of oxygen was evolved, when by the mercury test no free hypochlorous acid could be detected. The liquid still bleached slowly, but not so vigorously as before. 10 c.c. when tested with standard potassic hydrate solution contained as much free acid as was equivalent to 0·0302 gram of chlorine, but when tested with standard silver nitrate solution, it yielded chloride corresponding with 0·0224 gram of chlorine only. 10 c.c. treated with the zinc-copper couple, and then the total chlorine as chloride estimated, contained 0·0292 gram of chlorine. These last two numbers are nearly in the ratio 3 : 4, for in that case the weights would be 0·0219 (instead of 0·0224) to 0·0292. Thus it is clear that about three-fourths of the acid present was in the form of hydrogen chloride, and one-fourth as an oxidised chlorine acid (that is chloric acid), and the slow bleaching action of the solution can be accounted for by the presence of chloric acid. Now, it can be calculated that 60 c.c. of the acid of this strength would contain roughly about 60 c.c. of oxygen in the hypochlorous acid, but only 18 c.c. were evolved, which is a little more than a fourth of the total amount. By the action of concentrated hydrochloric acid and potassic iodide, distinct amounts of iodine were liberated, indicating again the existence of chloric acid in solution. The equation for the decomposition of hypochlorous acid which will therefore be most nearly in accordance with the above numbers is $4HClO = HClO_3 + 3HCl + O$. It is quite possible that the reaction representing the decomposition of hypochlorous acid by the action of strong diffused light is not very sharply defined, but for working purposes it may be taken that solutions of hypochlorous acid of the strength above indicated, when thus exposed, undergo the above decomposition. That this reaction partly depends on the strength of the acid which is being decomposed, is shown by the following experiment:—A dilute solution of distilled hypochlorous acid containing in 10 c.c. of solution 0·0293 gram of chlorine as hypochlorous acid, as judged both by reduction with the zinc-copper couple, and by the liberation of iodine from potassic iodide, that is, of practically the same strength as used in the previous experiment, was diluted with distilled water, 50 c.c. of the acid being taken to 30 c.c. of water, and the diluted acid exposed to strong tropical sunshine for seven days. Only a small amount of oxygen gas was evolved during the decomposition. At the end of seven days the solution had almost entirely lost its power of bleaching, and no trace of hypochlorous acid could be detected by the mercury reaction. A volume representing 10 c.c. of the original hypochlorous acid, after this exposure, required an amount of standard alkali solution equivalent to 0·0292 gram of chlorine, but by standard silver nitrate solution, the amount of chlorine present as chloride was found to be 0·0234 gram. The same volume of solution reduced by the zinc-copper couple, and tested with standard silver nitrate solution then contained 0·0289 gram of total chlorine as chloride, indicating also that there had been chloric acid present in this case. These figures stand nearly in the ratio of 4 to 5, and would indicate a probable decomposition according to the equation $5HClO = 4HCl + HClO_3 + O_2$. Further, the intensity of the light appears to exert a distinct influence on the character of the decomposition, for two samples of the same solution of hypochlorous acid were decomposed by the action of light, and while in one case 100 c.c. of the liquid exposed to the full blaze of tropical sunshine gave off 50·6 c.c. of oxygen, 100 c.c. of the same solution exposed merely to strong diffused daylight gave off only 20·0 c.c. of oxygen.

It might perhaps be imagined that even chloric acid itself would not be stable in the conditions worked under in these experiments, for it is stated that concentrated solution of chloric acid forms perchloric acid on being exposed to light. To test whether this was the case or not, some solutions of chloric acid of definite strengths were prepared and exposed to the action of strong tropical sunlight. Solutions of chloric acid containing a fifth of a mol. in grams, a tenth of a mol., a twentieth of a mol., and a thirtieth of a mol. in a litre of water, were prepared and placed in flasks, so that the solutions nearly filled them, the flasks being provided as usual with delivery tubes. They were then exposed to the action of sunlight. In no case was any oxygen evolved, proving that if any decomposition was occurring, it must be the entire conversion of the chloric into perchloric acid by such a reaction as $4HClO_3 = 3HClO_4 + HCl$. To estimate if any change of this kind had gone on, the amount of chlorine as chloride was determined in the solutions at different periods of the exposure. At first, all the solutions were entirely free from chloride, but after two days' exposure, that is, to about 16 hours' full sunshine, the N/5 and N/10 solutions showed distinct turbidity with silver nitrate solution, but N/20 and N/30 solutions showed little or no change. After six days' exposure, during which there were 48·4 hours of bright sunshine out of a possible duration of 68·4 hours, there was in all cases slight evidence of change, but it was found that less than a fiftieth of the chloric acid had been changed to hydrochloric acid. After 15 days' exposure, during which there were 134·2 hours of bright sunshine out of the possible amount of 184 hours, in the various solutions the proportions of chloride to the original chlorate were as follows:—

In the N/5 solution, 3·2 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

In the N/10 solution, 2·1 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

In the N/20 solution, 3·1 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

In the N/30 solution, 2·3 atoms of chlorine as chloride to 100 atoms of chlorine as chlorate.

The decomposition of chloric acid in dilute solutions under the influence of sunlight is, therefore, so small that its change in the previous experiments with chlorine water may be practically neglected, and it may be considered that the change in the experiments made with chlorine water by the action of light ends with the production of chloric acid.

The results of the above experiments may be thus briefly summarised:—Chlorine has very little action on water, even in the direct rays of a tropical sun, unless the water is in relatively enormous excess, the amount of water required being about 400 times as large as that indicated by theory, before even moderate action takes place. The main reaction which takes place between a large excess of water and small amounts of chlorine in the full blaze of an Indian sun in the hot season of the year is that expressed by the equation $2H_2O + 2Cl_2 = 4HCl + O_2$. On the other hand, in feeble diffused light, the first action which takes place between water and chlorine may be expressed by the equation $H_2O + Cl_2 = HCl + HClO$, but the hypochlorous acid formed is, in its turn, decomposed by light with the formation of chloric acid, so that in diffused light or in light less brilliant than tropical sunshine, the final reactions become such as put forward by Popper, or such as—

$$4Cl_2 + 4H_2O = 4HCl + 4HClO,$$

and

$$4HClO = HClO_3 + 3HCl + O,$$

or, combining the two,

$$4Cl_2 + 4H_2O = 7HCl + HClO_3 + O.$$

It will be therefore seen that, in the first stages at all events, the action of chlorine on water is quite similar to the action of chlorine on dilute and cold solutions of sodic hydrate or potassic hydrate, and also that the second reaction between chlorine and water is very similar to the action of chlorine on more concentrated and hot solutions of the two hydrates.

XL.—*Notes on the Explosion of Sulphuretted Hydrogen and of the Vapour of Carbon Bisulphide with Air and Oxygen.*

By ALEXANDER PEDLER, F.I.C.

In carrying out certain gas analyses, it was found desirable to attempt to determine the amounts of sulphuretted hydrogen and of the vapour of carbon bisulphide in the presence of air by explosion with oxygen.

In the case of explosion of sulphuretted hydrogen with oxygen, Dalton has stated, "1 vol. of hydrosulphuric acid exploded with half a vol. of oxygen is completely converted into water and sulphur, because half a vol. of oxygen is exactly sufficient to convert the 1 vol. of hydrogen contained in 1 vol. of hydrosulphuric acid gas into water; with 1½ vols. of oxygen it is completely converted into water and 0·87 vol. (in reality 1 vol.) of sulphurous acid gas. In this case, 1 vol. of oxygen combines with one-sixth vol. of sulphur vapour to form 1 vol. of sulphurous acid gas; part of this, however, is absorbed by the water which is formed at the same time" ("Gmelin's Chem.," **2**, 197). But beyond these brief statements no details of such explosions appear to have been published. Similarly, in the case of explosions of carbon bisulphide vapour with oxygen, although the general phenomena are well known, the published results are almost wanting. Berzelius and Marcet say: "Its vapour (carbon bisulphide), mixed with oxygen gas, produces a most violent explosion . . . . The products of the combustion are always sulphurous and carbonic acids, or carbonic oxide if the supply of oxygen is too small to form carbonic acid" ("Gmelin's Chem.," **2**, 203).

The usual practice hitherto in gas analysis has been to determine the sulphuretted hydrogen, either by a bullet of manganese dioxide, moistened with phosphoric acid, or by the action of solution of cupric sulphate, whilst in the case of carbon bisulphide the best available method has perhaps been to absorb with alcoholic potash.

The results of explosions of these two sulphur compounds with air and oxygen, however, at once showed that besides the simple oxidation of the sulphur, hydrogen, and carbon to be expected by theory, there were secondary reactions going on, and the following experiments were made to endeavour to ascertain what was their nature. As the result of these experiments was rather exceptional, it is thought desirable to place the main facts on record. It may be here mentioned that all the experiments to be described were performed in one of McLeod's gas analysis apparatus, and all the gases were used in the moist state.

The cause of the secondary reactions was at once shown not to exist in the reaction between sulphuretted hydrogen and air and oxygen. This was proved by taking 2·63 vols. of air with 3·42 vols. of pure sulphuretted hydrogen and 12·59 vols. of pure oxygen. On explosion, the contraction equalled 5·13 vols., the sulphur dioxide 3·38 vols., and the residual nitrogen 2·19 vols. The equation $2H_2S + 3O_2 = 2SO_2 + 2H_2O$ requires that the contraction should be one and a half times as great as the volume of sulphuretted hydrogen used, and $3·42 \times \frac{3}{2} = 5·13$. It may, therefore, be assumed that, if necessary, this process for the estimation of gaseous sulphuretted hydrogen can be used with fair accuracy.

The case is, however, very different with the vapour of carbon bisulphide. The method of procedure in the experiments about to be described was as follows:—A volume of air was taken and measured in the eudiometer tube. It was then passed back to the laboratory tube, where it was saturated with the vapour of some carbon bisulphide which had been specially purified. After measuring the volume of air, plus the carbon bisulphide vapour, it was mixed with a considerable excess of oxygen, and exploded at a tension which was measured. The contraction, the volume of sulphur dioxide, the carbon dioxide, and the residual nitrogen were then, in most of the experiments, measured. By the equation $CS_2 + 3O_2 = CO_2 + 2SO_2$, the amount of contraction should equal precisely the volume of the carbon bisulphide vapour used, whilst the volume of carbon dioxide should be equal to that of the carbon bisulphide, and that of sulphur dioxide should be twice as great as the carbon bisulphide vapour.

The following is a typical result of the explosion of vapour of carbon bisulphide with air and excess of oxygen:—2·42 vols. of air were mixed with 3·02 vols. of carbon bisulphide vapour, and then with 9·96 vols. of pure oxygen, and the mixture exploded. The contraction on explosion was 3·61 vols., the sulphur dioxide and carbon dioxide together equalled 9·00 vols., and the amount of nitrogen left behind was 1·67 vols. Now, the original volume of air would have contained 1·914 vols. of nitrogen, so there had been a very distinct disappearance of this gas during the explosion; on the other hand, the volume of $CO_2 + SO_2$ together should have equalled 9·06 vols., and only 9·00 vols. were found. The contraction should have equalled 3·02 vols., or the volume of the carbon bisulphide vapour, whilst it actually measured 3·61 vols. There had thus clearly been a disappearance of nitrogen and of either sulphur dioxide or carbon dioxide, and, probably, of oxygen as well, in this experiment.

In a second experiment, 2·14 vols. of air were mixed with 4·22 vols. of carbon bisulphide vapour, and 19·99 vols. of oxygen were added. The mixture was exploded at a tension of 150 mm., when a bright blue flash and very decided explosion occurred, and a small, white deposit occurred in the tube. The contraction, which was measured about five to ten minutes after the explosion, equalled 5·29 vols., while the amount of sulphur dioxide was 7·83 vols., that of carbon dioxide was 4·09 vols., and 1·57 vols. of nitrogen were left.

In this experiment, it will be seen that the contraction was 1·07 vols. in excess of theory, the volume of sulphur dioxide found was less than the theoretical amount by 0·61 vol., and 0·123 vol. of nitrogen had diappeared.

In another experiment, which gave results differing even more exceptionally from theory than the last two, 2·19 vols. of air were mixed with 5·88 vols. of carbon bisulphide vapour, 24·71 vols. of oxygen were added, and the tension of the gases was brought to about 165 mm., when the explosion was made, giving a bright, sharp, purple-coloured flash. After the explosion, a small amount of white deposit was seen in the tube, and the contraction, instead of ceasing when the temperature of the gas became constant, went on continuously for about 50 minutes, when it became exceedingly slow. A single drop of water was then allowed to enter the eudiometer tube, when at first a distinct expansion took place, showing probably either that the gases had become free from moisture, and were expanding from the tension due to the aqueous vapour, or that there was some substance present in the eudiometer tube which was decomposed by the action of water evolving gases, or some substance that evolved heat on the addition of the water. After this, contraction recommenced, and. even after the lapse of considerably more than an hour, the contraction of the volume of the gas or absorption was still going on, though very feebly. This continued contraction, which was so very largely developed in this case, was found not to be an isolated phenomenon, and in several other similar experiments, contraction has gone on for very considerable periods after the explosion—even after allowing ample time for the gases to cool down to their original temperature after the explosion.

The total contraction which was measured in this experiment was 16·25 vols., whilst the sulphur dioxide produced measured 4·74 vols., and the carbon dioxide 5·50 vols. Here it will be seen the amount of contraction was 16·25 vols. instead of 5·88 vols., or nearly three times as great as theory; the sulphur dioxide was 4·74 vols. instead of 11·76 vols., or about one-third of the theoretical amount, whilst the carbon dioxide was 5·50 vols. instead of 5·58 vols. There was thus a comparatively excessive contraction, and a similarly large loss of sulphur dioxide.

The behaviour of the gases in this experiment, after explosion, at once suggested a possible explanation of the unusual phenomena obtained in these experiments. In the first two cases it will be seen that less nitrogen was found at the conclusion of the experiment than there was at starting—proving that, as one of the results of the explosion, nitrogen had been oxidised. This oxidation appears to be similar to that found to be the case many years ago by Bunsen, when nitrogen in presence of oxygen was exploded with considerable volumes of detonating gas ("Bunsen's Gasometry," English Edition, p. 58). The oxide or oxides of nitrogen formed being, then, in presence of the sulphur dioxide, produced from the carbon bisulphide and of the moisture in the eudiometer tube (for the gases were always measured in a moist state in these experiments, and the eudiometer was kept moist) and also of free oxygen, it will be seen all the materials necessary for the preparation of sulphuric acid, on a small scale, were present in the tube. It was noticed that during the contraction, which extended over more than an hour in the last case, there was evidently some substance produced which was deposited on the sides of the tube, and also, after the analysis, it was found that the eudiometer tube, when washed out with water, had a very decidedly acid reaction. The possible explanation, therefore, which is suggested is that a slow formation of sulphuric acid was going on in the tube; and this would also account for the very acid reaction possessed by the washings from the eudiometer tube. In the second and third experiments, it will also have been noticed that a white deposit occurred in the tube; this was quite an ordinary occurrence in those experiments, and, so far as could be judged, the only possible explanation of the deposit is that this consisted of a small amount of some such compound as the so-called lead-chamber crystals, which, in the comparative absence of moisture, had not decomposed.

A series of experiments was made to see if there was any definite relation between the amount of contraction and certain varying conditions of the experiments, and the only general but rather rough result which could be obtained was that the amount of contraction became greater when the volume of oxygen was increased within certain limits, and, conversely, the volume of sulphur dioxide, which could be measured, decreased. This is shown in the following table, which contains several other analyses. The third of the above experiments gave such distinctly anomalous results, that it and some others made have not been included in calculating out the general results given on p. 630. In the table, the results are arranged according to the increase in the ratio of oxygen to the combustible gas.

These figures, it will be seen, indicate that the volume of carbon dioxide obtained by the combustion of carbon bisulphide in oxygen is, as might be expected, in accordance, practically, with theory; but, on the other hand, the contraction on explosion is always much greater than it should be, whilst the volume of sulphur dioxide is correspondingly smaller. The figures representing the excess of contraction on explosion and the sulphur dioxide are naturally not strictly complementary, for if the above suggested or possible explanation of the anomalous results be accepted, it will be seen in the formation of sulphuric acid, in addition to the sulphur dioxide, the volume of oxygen which disappears will form part of the contraction; the oxides of nitrogen which are formed may act also on the mercury in the eudiometer. In the second case of the possible formation of the lead-chamber crystals ($HSO_4 \cdot NO$), a similar effect will be obtained, for the contraction in this case should much more than exceed the volume of sulphur dioxide which condenses from the additional disappearance of both oxygen and the oxide of nitrogen and the vapour of water, whilst if both sulphuric acid and nitrosyl sulphate were formed as the result of any explosion, the actual cause of the whole contraction may be expected to become very complicated. In view,

Number of volumes of air.	Number of volumes of carbon bisulphide vapour.	Number of volumes of oxygen added.	Tension at moment of explosion in mm.	Contraction in volumes.	Volumes of sulphur dioxide.	Volumes of carbon dioxide.	Ratio of oxygen used to volume of vapour of carbon bisulphide (equal 1).	Ratio of contraction to volume of vapour of carbon bisulphide (equal 1).	Ratio of sulphur dioxide to vapour of carbon bisulphide (equal 1).	Ratio of carbon dioxide to vapour of carbon bisulphide (equal 1).
α. From 3 to 4 volumes of oxygen to 1 of carbon bisulphide.										
1·94	6·27	21·05	175	7·11	12·47	6·83	3·35	1·13	1·98	1·08
3·08	6·26	23·26	165	8·00	11·58	6·28	3·81	1·28	1·85	1·03
2·65	4·97	19·05	95	5·74	9·36	4·77	3·94	1·16	1·89	0·96
3·48	4·82	18·56	90	5·69	8·81	4·67	3·99	1·18	1·83	0·97
Mean ratios							3·77	1·19	1·89	1·01
β. From 4 to 4½ volumes of oxygen to 1 of carbon bisulphide.										
2·30	4·50	17·96	162	5·88	8·34	4·48	4·09	1·31	1·85	0·99
2·33	4·67	18·68	120	5·60	8·80	4·56	4·10	1·20	1·88	0·98
Mean ratios							4·10	1·26	1·86	0·99
γ. From 4½ to 5 volumes of oxygen to 1 of carbon bisulphide.										
2·40	5·70	25·63	160	7·57	10·85	5·85	4·57	1·33	1·90	1·02
2·14	4·22	19·99	150	5·29	7·83	4·09	4·83	1·25	1·85	0·97
2·05	4·05	19·28	175	5·32	7·79	4·09	4·86	1·31	1·92	1·01
2·13	5·17	25·08	175	6·70	10·00	5·12	4·94	1·30	1·93	0·99
Mean ratios							4·80	1·30	1·90	1·00
δ. From 5½ to 6 volumes of oxygen to 1 of carbon bisulphide.										
2·23	4·18	23·28	170	5·53	7·99	4·22	5·68	1·33	1·91	1·01

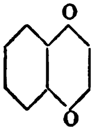
therefore, of these complications, it was not thought necessary to push the experiments any further than has been done.

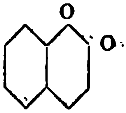
The explanation of the oxidation of the nitrogen in these experiments, even though comparatively low tensions were employed in the explosions, is probably to be found in the fact that carbon bisulphide, in its combination with oxygen, yields such a large amount of heat, and, therefore, produces such an excessively high temperature. Carbon bisulphide is well known to be an endothermic compound, or one which is formed from its elements with the absorption of a large amount of heat. As a liquid, when formed from its elements, it absorbs, according to Thomsen, no less than 19610 calories, and, when exploded with oxygen, this amount of heat, in addition to the heat of combination of both carbon and sulphur with oxygen, will necessarily be liberated. Hence the temperature produced in these explosions with oxygen will be exceedingly high.

XLI.—*A Third Naphthaquinone.*

By RAPHAEL MELDOLA, F.R.S., and FRANK HUGHES.

OF the four naphthaquinones indicated by theory, viz.:—


I.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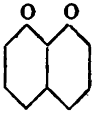
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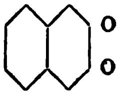

IV.

only the first and second are at present known, these being the familiar compounds α- and β-naphthaquinone respectively (Groves, this Journal, 1873, 209; and Stenhouse and Groves, *ibid.*, 1877, ii, 52). In 1885, Ekstrand made the important observation that heteronucleal di-derivatives of naphthalene of the form $\alpha'_1\ \alpha_1$ behaved in the same manner as ortho-derivatives (*Ber.*, 1885, 2881), a discovery which was confirmed and extended by Bamberger and Philip, in their interesting researches in connection with the constitution of acenaphthene and pyrene (*Ber.*, 1887, 237). This observation rendered possible theoretically the existence of a third ortho- (peri-) naphthaquinone, a compound which has not hitherto been prepared. By the action of nitric acid (sp. gr. 1·1) on acenaphthene, Quincke obtained two years ago a nitro-naphthaquinone, which is no doubt the nitro-derivative of the periquinone (*Ber.*, 1888, 1460).

In a paper recently communicated to the Society (Trans., 1890, 393), we stated that by the action of fuming nitric acid on dibrom-α-naphthol we obtained, in addition to the monobromindone described in our paper, a small quantity of an insoluble bye-product, which was separated during the crystallisation of the crude indone from alcohol. This compound is formed only in very small quantity, but is invariably present in the crude product. We have in the course of our experiments accumulated just enough to enable us to confirm the statement that this insoluble residue consists of the missing peri-(γ-) naphthaquinone.

The insoluble residue obtained in the manner described was washed repeatedly with hot alcohol till free from all soluble matter. The product was then dried, and two specimens prepared for analysis, one by crystallisation from glacial acetic acid, in which it is but slightly soluble, and the other by crystallisation from nitrobenzene, in which it is more readily soluble. Both specimens were finally washed with alcohol and dried:—

I. 0·1294 gram gave 0·3577 gram CO_2 and 0·0450 gram H_2O.
II. 0·1468 „ „ 0·4072 „ „ 0·0574 „

	Calculated for $C_{10}H_6O_2$.	Found. I.	Found. II.
C..........	75·95	75·39	75·65
H	3·79	3·89	4·36

The quinone forms slender, pale-yellow needles, remarkably insoluble in most solvents, and having no definite melting point. Above 220°, it blackens and decomposes. The compound is not reduced by standing in aqueous sulphurous acid. Reduction was effected by heating the substance with glacial acetic acid and zinc-dust, and filtering the solution into water. The quinone dissolves very slowly on prolonged boiling with dilute caustic soda, the solution being reddish, and giving a yellowish, flocculent precipitate on the addition of hydrochloric acid. On adding phenylhydrazine to the solution of the quinone in glacial acetic acid, a red colour is at once developed, and reddish needles with a metallic lustre separate. This substance, which is probably an azo-compound, dissolves in aqueous alkalis with a reddish-brown colour, and is reprecipitated by acids.

Dihydroxynaphthalene.—The product of reduction of the quinone obtained in the manner described separates from the acetic acid solution on dilution with water, in the form of minute, whitish needles, which become slate-coloured by oxidation on exposure to the air. A, specimen prepared for analysis by being collected, washed with water, and dried, gave the following result:—

0·1159 gram gave 0·3194 gram CO_2 and 0·0484 gram H_2O.

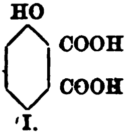
	Calculated for $C_{10}H_6(OH)_2$.	Found.
C	75·0	75·16
H	5·0	4·64

This dihydroxynaphthalene is distinguished by the following properties:—It is insoluble in hot water, and but slightly soluble in cold alcohol. Its solutions become violet on exposure to the air. A piece of white filter-paper wetted with the solution and exposed to the air gradually acquires an indigo-blue colour. The substance dissolves readily in cold aqueous caustic soda, or in dilute ammonia, the solution rapidly becoming reddish-violet by oxidation, and finally acquiring an indigo-blue colour. A solution of a chromate added to the acetic acid solution of the substance causes a violet coloration, which soon disappears, and the quinone crystallises out. Nitric acid immediately reconverts the dihydroxy-derivative into the quinone. The substance has no definite melting point, but it blackens and shrinks about 205°. The diacetyl-derivative was obtained by heating the substance for a few minutes with acetic anhydride and dry sodium acetate. On dilution with water, the substance separates out in the form of small, whitish, flattened needles collected into stellate bundles. After crystallisation from glacial acetic acid, the melting point was 226—227°. This diacetyl-derivative is only very sparingly soluble in alcohol. An analysis gave the result:—

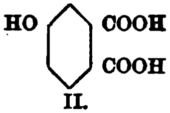
0·1434 gram gave 0·3626 gram CO_2 and 0·0620 gram H_2O.

	Calculated for $C_{10}H_6(O{\cdot}C_2H_3O)_2$.	Found.
C	68·85	68·95
H	4·92	4·80

The constitution of the dihydroxynaphthalene was proved by its behaviour on oxidation by means of hot alkaline permanganate. After removal of the excess of permanganate by ferrous sulphate and filtration, the alkaline solution was concentrated to a small bulk, acidified by dilute sulphuric acid, and extracted with ether. After the latter solvent had evaporated, there remained a small quantity of a crystalline residue, only just sufficient for purification and the determination of a melting point. After being twice crystallised from water, the melting point was 194—197°. Phthalic acid melts at 184°. Of the two hydroxyphthalic acids—

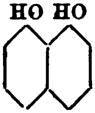


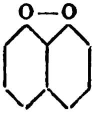
I.



II.

the first melts when rapidly heated at 196—200° (Jacobsen, *Ber*, 1883, 1965), and the second at 180—183° (Graebe, *Ber.*, 1885, 1130). Our acid, which gave the fluoresceïn reaction with resorcinol, agrees therefore most closely with formula No. I. This leads to the conclusion that the constitutions of the dihydroxynaphthalene and the quinone are:—





We thus have in this compound a type of a peroxide quinone as distinguished from a diketone.

We are at present unable to account for the formation of the quinone under the circumstances described. It is possible that during the bromination of *α*-naphthol a small trace of peri-monobrom-*α*-naphthol is produced, and that this, by the action of fuming nitric acid, furnishes the quinone. Experiments to test this suggestion, as well as to obtain the quinone by other methods, will be continued.

Finsbury Technical College.

XLII.—*Diethylphosphorous Acid.*

By T. E. THORPE, F.R.S., and BARKER NORTH, Associate of the Normal School of Science, South Kensington.

ETHYL alcohol and phosphorous oxide react upon each other at the ordinary temperature with such energy that the mixture inflames, but by surrounding the vessel containing the oxide with a mixture of ice and salt and allowing the alcohol to act slowly, drop by drop, the phosphorous oxide gradually dissolves, and a clear liquid is obtained. On distillation, the greater part of this liquid is found to boil constantly at 184—185°, a quantity of phosphorous acid remaining behind in the distilling flask. Analysis showed that the distillate so obtained was *diethylphosphorous acid.*

I. 0·3256 gram, after treatment with nitric acid by Carius's method, gave 0·2575 gram $Mg_2P_2O_7$.

II. 0·3841 gram gave 0·3048 gram $Mg_2P_2O_7$.

Phosphorus found.		Phosphorus calculated for $P(OC_2H_5)_2OH$.
I.	II.	
22·10	22·20	22·47

The main reaction proceeds in accordance with the equation

$$P_4O_6 + 8C_2H_5{\cdot}OH = 4P(OC_2H_5)_2OH + 2H_2O.$$

Diethylphosphorous acid is a colourless, mobile, slightly acid liquid, possessing a peculiar, penetrating, alliaceous odour. Its vapour is poisonous, and even small quantities produce headache and nausea. In an atmosphere of carbon dioxide, it boils constantly at 184—185°. Its relative density is 1·0749 at $\frac{15{\cdot}5^\circ}{4^\circ}$. It is readily decomposed by water forming alcohol and phosphorous acid:

$$P(OC_2H_5)_2OH + 2H_2O = 2C_2H_5{\cdot}OH + P(OH)_3.$$

This reaction accounts for the phosphorous acid which is always produced in the preparation of the substance.

Bromine acts upon diethylphosphorous acid with great violence. By cautiously adding bromine, drop by drop, to a weighed quantity of the well cooled liquid until it remained permanently coloured, it was found that 1 mol. of the diethylphosphorous acid required exactly 1 mol. of bromine to complete the decomposition. On heating the liquid, *ethyl bromide* boiling at 38—40° passed over, and the residue in the flask proved to be *metaphosphoric acid*, the silver salt of which was prepared and analysed.

Bromine acts on diethylphosphorous acid, therefore, according to the equation

$$P(OC_2H_5)_2OH + Br_2 = 2C_2H_5Br + HPO_3,$$

a reaction analogous to that by which phosphorous acid itself is converted into metaphosphoric acid by the action of bromine:

$$P(OH)_3 + Br_2 = 2HBr + HPO_3.$$

All the ethylphosphorous acids indicated by theory are now known. Monethylphosphorous acid, $P(OC_2H_5)(OH)$, was first obtained by Wurtz. The triethyl compound was first prepared by Railton (Trans., **7**, 216). The chloride of diethylphosphorous acid was obtained by Wichelhaus (*Ann. Suppl.*, **6**, 263) by the action of 1 mol. of phosphorus trichloride upon 2 mols. of ethyl alcohol: $2PCl_3$ +

$2C_2H_5OH = P(OC_2H_5)_2Cl + 2HCl$, and salts corresponding to the acid were prepared by Railton and Wurtz. Certain of these compounds, together with other alkyl-derivatives of phosphorous acid, have recently been examined by Jaehne (*Annalen*, **256**, 269).

XLIII.—*The Relative Antiseptic Powers of Isomeric Organic Compounds.*

By THOS. CARNELLEY, D.Sc., Aberdeen, and W. FREW, F.C.S., Dundee.

WITH the object of determining the influence of atomic arrangement on the antiseptic properties of organic compounds, we have investigated the relative antiseptic powers of a number of isomeric organic compounds, more particularly of di-derivatives of benzene.

The method of experiment was briefly as follows:—5 to 10 c.c. of Koch's sterilised peptogelatin* were placed in a small glass tumbler, about 2 inches in diameter and 1½ inch deep, and a known weight of the compound under investigation added. The vessel was very gently warmed in an oven, and stirred until the whole of the compounds had dissolved in the jelly;† it was then covered with paper and set aside until the jelly had completely solidified. After having been inoculated by exposure in a dusty room for 15 minutes, the cover being removed, it was re-covered and placed in a water-oven kept at a constant temperature of 16 to 18° C. (that is, several degrees below the melting point of the jelly), for six days. At the end of this time it was taken out, and the surface of the jelly carefully examined with a pocket lens to see whether any colonies of micro-organisms had formed. If no colonies appeared, then the experiment was repeated, using the same volume of jelly, but with a smaller quantity of the compound dissolved in it. On the other hand, if colonies appeared, the experiment was repeated with jelly containing a larger quantity of the substance. This was continued until a point was reached at which the weight of dissolved compound was just sufficient to prevent the appearance of colonies for six days under the above conditions. It was quite easy to hit the point so that a milligram more or less of the substance was sufficient to reverse the result.

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* Containing the juice of 1 lb. of lean meat, 10 grams of peptone, 5 grams of common salt, and 100 grams of French leaf gelatin to 1 litre of water, and, after heating, carefully neutralised with sodium carbonate, and filtered.

† Any slight infection of the jelly which might occur at this stage was of no consequence in view of the subsequent exposure to dusty air.

In the case of some of the compounds, namely, acids and phenols, the calculated quantity of sodium carbonate was also added in order to convert them into the sodium compounds, and thus render them more easily soluble in the jelly. The results given in the following table represent the weights of the respective compounds per litre of jelly required to prevent the appearance of colonies of micro-organisms for six days at 16 to 18°.

	Grams per litre of jelly required to prevent the appearance of colonies of micro-organisms for 6 days at 16—18°.		
	Ortho-.	Meta-.	Para-.
Sodium hydroxybenzoates, $C_6H_4(OH)\cdot COONa$	11·6	67·2	more than 162·1
Sodium phthalates, $C_6H_4(COONa)_2$..........	63·2	—	50·6
Nitrotoluenes, $C_6H_4(CH_3)\cdot NO_2$...............	more than 22·0	—	22·0
Sodium nitrobenzoates, $C_6H_4(NO_2)\cdot COONa$ ..	101·6	12·1	7·7
Sodium dihydroxybenzenes, $C_6H_4(ONa)_2$.....	less than 3·9	8·1	3·6
Amidotoluenes, $C_6H_4(CH_3)\cdot NH_2$	more than 1·4	—	1·4
Nitranilines, $C_6H_4(NO_2)\cdot NH_2$	—	0·84	0·50
Nitrobenzaldehydes, $C_6H_4(NO_2)\cdot COH$	0·30	—	0·24
Sodium nitrophenol, $C_6H_4(NO_2)\cdot ONa$........	1·72	0·28	0·12
Potassium nitrophenol, $C_6H_4(NO_2)\cdot OK$	0·90	—	0·12

	Grams per litre of jelly required to prevent the appearance of colonies of micro-organisms for 6 days at 16—18°.	
Sodium α-naphthol, $C_{10}H_7\cdot OH$....	0·084	
„ β- „ „	0·230	
Succinic acid, $C_4H_6O_4$	66·0	
Methyl oxalate, $C_4H_6O_4$	10·4*	
Sodium mesaconate, $C_5H_6O_4$	190·0	did not prevent the appearance of micro-organisms.
„ itaconate, „	190·0	

In three cases, viz.: sodium para-hydroxybenzoate, sodium itaconate, and sodium mesaconate, the quantity of substance required was so great as to prevent the jelly from solidifying, and yet was not sufficient to prevent the appearance of colonies. We have frequently observed in these, and also in the case of inorganic salts, that when a substance has to be used in such quantity as to prevent the jelly from setting, that substance is practically non-antiseptic.

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* Methyl oxalate is decomposed by water into methyl alcohol and oxalic acid, and no doubt the same decomposition would occur on dissolving in the jelly, so that this number will really refer to a mixture of the alcohol with the acid.

In most cases the development of moulds appeared to be prevented more easily than that of bacteria.

In the experiments with terephthalic acid, a peculiar odour of bitter almonds was noticed whenever colonies formed on the jelly. The jelly had no such odour before the colonies appeared. About 20 grams of terephthalic acid, in the form of sodium salt, per litre of jelly appeared to be most favourable for the development of this odour. Its occurrence would seem to indicate the reduction of the terephthalic acid to benzaldehyde. Jelly containing resorcinol, and in which colonies had developed, gave a characteristic yellow fluorescence when dissolved in hot water, an effect which was not observed unless micro-organisms had grown on the jelly containing the resorcinol.

The above table, so far as it goes, would seem to show that, as regards di-derivatives of benzene:

The para- (or most symmetrical and, as a rule, the least easily fusible and least soluble) *compounds are usually more powerfully antiseptic than the corresponding ortho- and meta-compounds.*

The hydroxybenzoates are, however, very marked exceptions to this rule. Curiously enough, the hydroxybenzoic acids are also the most marked exceptions to the rule which was shown by Carnelley and Thompson (Trans., 1888, **53**, 782), to be of almost general application, namely, that of two or more isomeric compounds the most easily fusible is also the most easily soluble; for the ortho-acid (salicylic acid), which is the most easily fusible, is the least soluble, and the para-acid, which is the least fusible, is the most soluble.

The ortho-dihydroxybenzene (pyrocatechol), in the form of the sodium compound, is also a possible exception to the above rule as regards antiseptic power.

In the above table, the di-derivatives of benzene are arranged in the order of the antiseptic power of the para-compounds, and it will be seen that the corresponding meta-compounds follow the same order, whereas, the ortho-compounds do not, or only to some extent. On the whole, compounds containing the COOH-group have, as a rule, a comparatively low antiseptic power. On the other hand, phenols and nitro-compounds appear to have a relatively high antiseptic power, so that in the above derivatives of benzene this property culminates in para-nitrophenol. The naphthols, and especially α-naphthol, are also very powerful antiseptics.

It must be understood that we do not wish to imply that these relations hold beyond the compounds we have investigated or the extent indicated, as the data are not sufficient to show whether the relations are of general application or not. They are, however, entirely in accord with the determinations recently made by Wolcott Gibbs and Hare (*Amer. Chem. J.*, **11**, 435), in regard to the action of the three nitrophenols, the three nitranilines, the three amidobenzoic acids, and the three nitrobenzoic acids, when injected into the veins of dogs.

In conclusion, we may say that the experimental part of our investigation was completed two years ago, but pressure of other work prevented its publication until now.

XLIV.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

No. I. *On Tertiary Butyl Mercaptan.*

By LEONARD DOBBIN, Ph.D.

THE known readiness with which zinc oxide acts on tertiary butyl iodide, as described in a previous paper communicated to this Society (Trans., 1880, 239), led the author, when in search of a method for the preparation of tertiary butyl sulphide, to try the action of zinc sulphide on the same iodide. It should be mentioned that the experience with zinc oxide, which yielded as chief products zinc iodide, water, and triisobutylene, did not seem to give much promise of reaching the desired result with the sulphide. On heating a mixture of the substances, however, on a small scale, unmistakable evidence of the formation of an organic sulphur compound was afforded by the extremely unpleasant and characteristic odour produced.

Various experiments were then made on a larger scale, but considerable difficulties were met with before the conditions for obtaining the best results were ascertained. It was found, for instance, that the extent to which the iodide underwent decomposition depended very greatly upon the sample of zinc sulphide employed; although the different experiments were made under conditions which were otherwise similar. With one commercial sample, the removal of iodine from the iodide became complete very rapidly, whilst with others it was found impossible to accomplish complete decomposition.

The first method employed for carrying out the reaction was as follows:—50 grams of tertiary butyl iodide were mixed with

200 grams of nearly anhydrous alcohol; 20 grams of (almost white) commercial zinc sulphide were added, and after standing for a few hours in the cold, the mixture was heated in a flask with a reflux condenser for about six hours. The alcohol was then distilled off as completely as possible by means of a water-bath, and the distillate diluted with about twice its own volume of water. A small portion separated out as a layer on the top of the aqueous alcohol. This was separated, dried over calcium chloride, and fractionated. It began to boil at about 65°, and the boiling point gradually rose to 100°, below which temperature more than half distilled over. At 107°, the distillation practically ceased, and almost nothing came over till 170° was reached. Then between 180° and 190°, nearly all the remainder distilled; at about 190°, decomposition, with darkening, began.

On repeatedly fractionating the fraction boiling at the lowest temperature, a large proportion of it was found to boil between 65° and 70°. This portion was quite free from iodine, and was sealed up for analysis. Its low boiling point seemed to indicate that it could not be tertiary butyl sulphide.

The normal sulphide boils at 182° (Grabowsky and Saytzeff, *Annalen*, **171**, 254); isobutyl sulphide boils at 170·5° (Beckmann, *J. pr. Chem.* [2], **17**, 446); secondary butyl sulphide boils at 165° (Reymann, *Berichte*, **7**, 1288).

Analyses gave numbers which correspond with the composition of tertiary butyl mercaptan:—

I. 0·2262 gram substance gave 0·4405 gram CO_2 and 0·2187 gram H_2O.

II. 0·2306 gram substance gave 0·4481 gram CO_2 and 0·2215 gram H_2O.

	Calculated for $(CH_3)CSH$.	Found.	
		I.	II.
C	53·33	53·11	52·99
H.........	11·11	10·74	10·67
S	35·55	—	—

In several subsequent experiments, made in exactly the same way, with other commercial samples of zinc sulphide, and also with a special laboratory preparation, the product was not in any case obtained free from iodine.

By a simplification of the foregoing method complete removal of the iodine and uniform results were obtained.

Preparation of Tertiary Butyl Mercaptan.

The zinc sulphide to be employed was precipitated from the aqueous solution of zinc sulphate by passing in sulphuretted hydrogen, ammonia being added from time to time to prevent the liquid from becoming so strongly acid as to prevent further action of the sulphuretted hydrogen. Owing to the great difficulty of efficiently washing the bulky precipitate of freshly-prepared zinc sulphide, the precipitate was at first only partially washed. Then it was dried at the ordinary temperature (whereby its bulk became very greatly decreased), finely powdered, thoroughly washed with water to remove ammonium sulphate, and again dried at the ordinary temperature. 20 grams of this zinc sulphide were heated in a retort on a water-bath with 50 grams of tertiary butyl iodide, till (at about 45°) a manifest action set in. To prevent loss of the very volatile product of the action, the retort was connected with a U-tube placed in a freezing mixture. The digestion was afterwards carried on at a gentle heat for about two hours, until rapid evolution of sulphuretted hydrogen was observed. This gas was not given off at the beginning of the operation. The contents of the retort were then distilled off as completely as possible from a water-bath. The distillate, which was collected in a freezing mixture, was dried over calcium chloride and then fractionated. It was quite free from iodine. A large proportion of it was found to be of low boiling point, and a large fraction boiling between 65° and 67° was employed for analysis:—

0·1878 gram substance gave 0·3619 gram CO_2 and 0·1861 gram H_2O.

These numbers correspond to 52·55 per cent. carbon, and 11·01 per cent. hydrogen, whilst tertiary butyl mercaptan requires 53·33 per cent. carbon, and 11·11 per cent. hydrogen.

This product was believed to be more nearly free from the product of high boiling point than that first analysed, although the percentage of carbon found was somewhat lower. The product of high boiling point is much richer in carbon than the mercaptan, so that the presence of a small quantity of it in the mercaptan would greatly raise the apparent carbon percentage of the latter. On the other hand, the extreme volatility of the mercaptan gave rise to slight loss at the commencement of each combustion, a fact which the smell of the mercaptan rendered unquestionable.

Properties of Tertiary Butyl Mercaptan.

Tertiary butyl mercaptan, obtained as described above, is a very volatile liquid, boiling at 65—67°. It solidifies to a white, semi-translucent mass when placed in a freezing mixture of snow and salt. It possesses an overpowering and characteristic disagreeable odour, which, however, is not so offensive as that of some of the lower homologues. It forms voluminous, white, insoluble compounds when mixed with aqueous solutions of mercuric chloride and of silver nitrate. The compound formed with the latter becomes black on standing for some hours, and quickly on boiling, owing to the formation of silver sulphide.

The fraction of high boiling point (over 180°), previously mentioned, was fractionated, and a small quantity of that boiling between 177° and 185° was used for combustion. Determinations of the carbon and hydrogen were made in order to find out the nature of the difference between the products of low and of high boiling points respectively, but the quantity available was too small to investigate the matter fully.

It was obvious from the formation of the mercaptan that some of the C_4H_9 groups of the original iodide must have lost hydrogen, and this fact, viewed in connection with the formation of tri-isobutylene, when zinc oxide acts on tertiary butyl iodido (Trans., 1880, 241), rendered it highly probable that polymeric isobutylene derivatives might be formed here also. The evolution of sulphuretted hydrogen could also only occur by similar loss of hydrogen from C_4H_9-groups. The only other product likely to be formed is tertiary butyl sulphide, the boiling point of which would probably lie not much below 160°. The boiling point of tri-isobutylene is 177·5—178·5° (Lermontoff), so that a separation of these two substances, if mixed, would be extremely difficult with the small quantity which was available. The figures obtained on combustion gave a result which would represent a mixture of tertiary butyl sulphide and tri-isobutylene:—

0·182 gram substance gave 0·5227 gram CO_2 and 0·2161 gram H_2O.

	Calculated for.		
	$(C_4H_9)_2S$.	C_nH_{2n}.	Found.
C.............	65·75	85·71	78·31
H.............	12·32	14·28	13·19

This part of the subject is at present under investigation.

It is of interest in connection with the foregoing and with the known difference of behaviour towards reagents of the isobutyl and tertiary butyl iodides, to note that Grabowsky and Saytzeff (*Annalen*, **171**, 255), prepared isobutyl sulphide by acting on isobutyl iodide with an alcoholic solution of potassium sulphide; but in trying to carry out an analogous reaction with the tertiary iodide, they failed to obtain anything more than "traces of a liquid possessing the characteristic garlic odour, whilst the greater portion of the iodide decomposed into hydriodic acid and butylene." In view of the fact that alcoholic solution of potassium sulphide does not react in the usual way with the tertiary iodide, Saytzeff states (*ibid.*, **171**, 258) that a student (Ivanoff) was (in 1874) about to try the action upon the latter of the sulphides of other metals, in imitation of Butlerow's method for obtaining tertiary butyl cyanide, but apparently no results of any such experiments have been published.

Beckmann (*J. pr. Chem.*, [2], **17**, 446) mentions that by distilling isobutyl potassium sulphate with aqueous solution of potassium sulphide, besides isobutyl sulphide (B. P. 170·5°), he obtained another sulphur compound boiling at 88°, the nature of which he did not then know. The substance was most likely isobutyl mercaptan, which had been previously described by Humann (*Annalen*, **95**, 256) as a liquid boiling at 88°.

XLV.—CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF EDINBURGH.

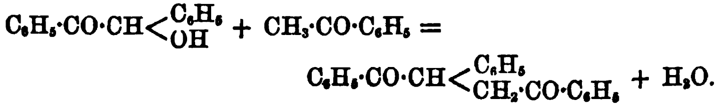
No. II. *On Desylacetophenone.*

By ALEX. SMITH, B.Sc., PhD.

IN the course of some experiments designed to see whether the benzoïn reaction was also applicable to a mixture of benzaldehyde with a ketone, an experiment with acetophenone gave a new substance of high melting point. Benzaldehyde, in presence of potassium cyanide, seemed to have no action on benzophenone, whilst with acetophenone an action indeed took place, but in an entirely unexpected direction. A substance having the formula $C_{29}H_{22}O_2$ was formed, probably according to the following equation:—

$$3C_6H_5\cdot COH + CH_3\cdot CO\cdot C_6H_5 = C_{29}H_{22}O_2 + 2H_2O.$$

As under the circumstances of the reaction it was certain that a large part of the benzaldehyde must have been converted into benzoïn before it had time to act, a trial was next made whether dilute potassium cyanide would not bring about condensation between molecular quantities of acetophenone and benzoïn alone. It was found to do so very easily, *desylacetophenone* being formed with elimination of 1 mol. of water:—



$$C_6H_5\cdot CO\cdot CH<\begin{matrix}C_6H_5\\OH\end{matrix} + CH_3\cdot CO\cdot C_6H_5 = C_6H_5\cdot CO\cdot CH<\begin{matrix}C_6H_5\\CH_2\cdot CO\cdot C_6H_5\end{matrix} + H_2O.$$

Desylacetophenone is the saturated derivative corresponding to the anhydroacetophenonebenzil of Japp and Miller (Trans., 1885, 34). In common with all 1 : 4-diketones, it is easily transformed into the corresponding furfurane, pyrroline, and thiophen derivatives. These substances, together with its behaviour towards hydroxylamine and phenylhydrazine, which conclusively prove its constitution to be that given, are described below.

In the application of this reaction to a mixture of benzoïn and acetone, no desylacetone could be discovered, if, indeed, any is formed. The only substance obtained was one corresponding to the above-mentioned high-melting product from acetophenone. The equation is exactly similar—

$$3C_6H_5{\cdot}COH + CH_3{\cdot}CO{\cdot}CH_3 = C_{24}H_{20}O_2 + 2H_2O.$$

I hope shortly to be able to describe the properties of these compounds, the investigation of which is almost completed, and postpone therefore all details as to their preparation till then.

Desylacetophenone, $C_{22}H_{18}O_2$.

Desylacetophenone is prepared by boiling 18 grams of acetophenone and 31 grams of benzoïn with 4 grams of potassium cyanide in a mixture of 75 grams of water and 75 grams of alcohol, using a reflux condenser. If the benzoïn does not completely dissolve at first, a little more alcohol must be added. If these proportions are departed from, or larger quantities used at one time, the yield may be seriously affected. When other conditions were tried, a curious amorphous substance was sometimes produced which could only be induced to crystallise by shaking its saturated solutions. It was found to be a mixture of desylacetophenone with benzoïn; these could not be separated by any number of recrystallisations from alcohol or acetic acid. Separation could only be effected by boiling with very large quantities of water, in which benzoïn is very slightly soluble, whilst desylacetophenone is insoluble. After half an hour, the desylacetophenone begins to separate out as an oil. After an hour and a quarter, the boiling is interrupted, the oil allowed to settle, and the liquid poured off. The oil soon solidifies to a mass of crystals, which, after standing some hours, is spread on porous plates to free it from any oil still mixed with the crystals. It is then boiled with alcohol, and filtered from a quantity of the substance $C_{29}H_{22}O_2$, which is formed at the same time according to the equation first given. On cooling, the alcoholic solution deposits yellowish, monoclinic crystals of desylacetophenone. A further portion separates from the mother liquor on standing, and is treated in the same way. The yield is about 18 grams. On recrystallisation from alcohol and acetic acid, it becomes colourless, and melts at 126°.

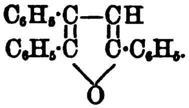
Analysis:—

0·2155 gram substance gave 0·6653 gram CO_2 and 0·1141 gram H_2O.

	Found.	Calculated for $C_{22}H_{14}O_2$.
C	84·19	84·07
H	5·88	5·73

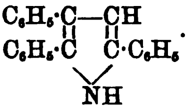
It is freely soluble in boiling alcohol and acetic acid, but much less so in the cold, and is also soluble in ether, chloroform, and benzene. It is not affected by boiling with alkalis, dilute acids, or even by strong hydrochloric acid. Acetic anhydride has no action on it, and it does not take up bromine in chloroform solution. As a 1 : 4-diketone, it is easily transformable into triphenylfurfurane.

Triphenylfurfurane,



As strong hydrochloric acid did not effect this transformation, the desylacetophenone was dissolved in concentrated cold sulphuric acid, allowed to remain for two hours, and the whole then poured into water. A viscid mass separated; when the water had become clear, it was poured off, and the amorphous deposit was dissolved in boiling alcohol. On cooling, the alcoholic solution gave beautiful needles of triphenylfurfurane melting at 92°. The yield is good. The substance is identical with that obtained by Japp and Burton (Trans., 1887, 430) by boiling anhydroacetophenonebenzil with hydriodic acid, and subsequently found by Japp and Klingemann (*Berichte*, **21**, 2933) to be triphenylfurfurane.

Triphenylpyrroline,



Desylacetophenone is sealed up, with excess of alcoholic ammonia, in a tube and heated for 4—5 hours at 150°. The warm alcoholic solution, diluted with a little water, on cooling deposits triphenylpyrroline in tufts of slender, white needles. After recrystallisation in the same manner, it is pure, and melts at 140—141°. It gives the pyrroline reaction.

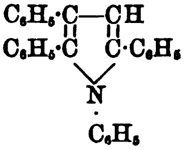
Analysis :—

0·2645 gram substance gave 0·8695 gram CO_2 and 0·1441 gram H_2O.
0·3340 „ „ 13·2 c.c. nitrogen at 15° and 715 mm.
bar. = 15·37 milligrams N.

	Found.	Calculated for $C_{22}H_{17}N$.
C	89·65	89·49
H	6·05	5·76
N	4·6	4·74

It is very soluble in alcohol, ether, light petroleum, and acetic acid. It does not dissolve in alkalis or acids. The crystals show a violet fluorescence, like some anthracene derivatives ; this is not diminished by repeated recrystallisations from various media, and cannot, therefore, be due to an impurity. An isomeride of this substance *aa'*-N-triphenylpyrroline (m. p. 228—229°) was made by Kapf and Paal (*Berichte*, 21, 3062) by the distillation of the corresponding carboxylic acid over lime. They found along with it a smaller quantity of a substance having the same composition but melting at 140—142°, and made the suggestion that this might possibly be an isomeride formed by a rearrangement of the phenyl-groups owing to the distillation over lime. This supposition is evidently correct, for the substance is, in the main, identical in its properties (so far as they give them) with the *aa'*-*β*-triphenylpyrroline described here. They state that the crystals were "bluish coloured," and again that the recrystallised substance, as analysed, was "*nearly* colourless." As a matter of fact, the above-mentioned fluorescence gives the substance a dirty-bluish tinge when seen at a distance, although it is perfectly pure. The only point of difference is that their pyrroline derivative is said to crystallise from acetic acid in "flat needles or plates." The present one crystallises from it in tufts of fine, silky needles.

aa'β-N-Tetraphenylpyrroline,



Three grams of desylacetophenone and 1 gram of aniline are boiled in glacial acetic acid solution for three to four hours, when the solid mass of tetraphenylpyrroline, which has separated out, is freed from the mother liquor and recrystallised from acetic acid. It forms white, silky needles melting at 196—197°

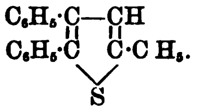
Analysis:—

0·4932 gram substance gave 16·5 c.c. nitrogen at 19° C. and 758 mm. bar. = 19·26 milligrams N.

	Found.	Calculated for $C_{28}H_{21}N$.
N	3·9	3·8

It is very slightly soluble in cold, moderately soluble in hot alcohol or acetic acid. It is soluble also in ether and benzene. It gives the pyrroline reaction.

Triphenylthiophen,



Five grams of desylacetophenone and 2 grams of phosphorous pentasulphide are heated in a test-tube at 150° till the reaction seems to be completed. This occurs after a few minutes. The contents of the tube are then boiled up with alcohol and the solution filtered, and allowed to cool, when it deposits plates or silky-white needles of triphenylthiophen. These are recrystallised several times from alcohol and from acetic acid, and, when pure, melt at 127°.

In sulphuric acid solution, with a little isatin, it gives, after standing some time, a greenish-yellow coloration. Diphenylthiophen gives a green. The Laubenheimer reaction (with phenanthraquinone) gives also a greenish-yellow coloration. The alteration in colour with the addition of phenyl-groups is interesting in this case also. Dimethylthiophen gives a violet colour, diphenylthiophen a green, whilst triphenylthiophen is seen to give a greenish-yellow.

It is extremely soluble in benzene, soluble in hot alcohol and acetic acid, less soluble in the cold, and quite insoluble in water. It is not volatilised in a current of steam.

Action of Phenylhydrazine on Desylacetophenone.

Under ordinary conditions, phenylhydrazine seems to have no action on desylacetophenone. On being mixed with phenylhydrazine in alcoholic solution and boiled, or even heated at 150° in a sealed tube, the original substance was always recovered unchanged. It is only in glacial acetic acid solution that any action takes place.

Tetraphenyldihydro-oiazine, $C_{28}H_{22}N_2$.

Ten grams each of desylacetophenone and phenylhydrazine are dissolved in about 70 grams of glacial acetic acid, and the whole warmed slowly by a very small flame. The flask is shaken from time to time till everything has dissolved, and the warming is continued till a separation of yellow needles, which soon begins, seems to have reached a maximum. It is now allowed to cool, when an almost quantitative yield of the new compound is obtained. The substance is purified by recrystallisation from alcohol, from which it separates in tufts of beautiful, yellow needles melting at 149°. When impure, it rapidly becomes brown on exposure to light. Analysis shows that 2 mols. of water have been eliminated in the reaction.

$$C_{22}H_{18}O_2 + C_6H_5N_2H_3 = C_{28}H_{22}N_2 + 2H_2O.$$

0·2229 gram substance gave 0·7113 gram CO_2 and 0·1214 gram H_2O.

0·4576 gram substance gave 29 c.c. nitrogen at 14° C. and 751 mm. bar.

	Found.	Calculated for $C_{28}H_{22}N_2$.
C	87·03	87·04
H	6·03	5·70
N	7·4	7·25

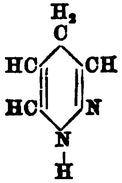
This reaction with phenylhydrazine, with loss of 2 mols. H_2O, seems to be general for *unsymmetrical* 1 : 4-diketones. Paal finds, for example (*Berichte*, **17**, 914), that acetophenoneacetone,

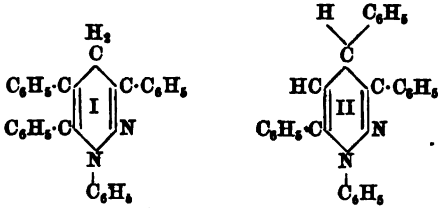
$$C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH\ {\cdot}CO{\cdot}CH_3,$$

yields a corresponding compound, to which, however, he gives no name. Symmetrical ones, on the other hand, such as acetonylacetone, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}CH_3$ (*ibid.*, **18**, 60), diphenacyl, $C_6H_5{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO{\cdot}C_6H_5$ (*ibid.*, **21**, 3056), and ethyl diacetosuccinate (*ibid.*, **17**, 2051), give diphenylhydrazones. In the case of the unsymmetrical compounds, one carbonyl-group is probably more easily attacked than the other, and the resulting monophenylhydrazone seems to form an internal anhydride more easily than a diphenylhydrazone.

Ethyl diacetosuccinate reacts, indeed, also as losing $2H_2O$ (Knorr, *Berichte*, **18**, 304), and Knorr supposes the product to contain a ring composed of two nitrogen- and four carbon-atoms, to which he gives the name *pyridazine*. In a later paper, however (*Annalen*, **236**, 295), he recognises this compound as a pyrroline-derivative, and ethyl diacetosuccinate follows, therefore, strictly the above rule as to symmetry.

Ach (*Annalen*, **253**, 46) revives the name pyridazine for substances containing such a ring, and following this nomenclature, the derivative from desylacetophenone should be called *tetraphenylpyridazine*. It seems better, however, to make use at once of the system of naming nitrogen rings proposed by Widman (*J. pr. Chem.*, **38**, 185), as it expresses the constitution of each compound very simply, and I understand is to be used in future editions of Beilstein's "Handbuch der organischen Chemie." A ring containing four carbon-atoms, and two nitrogen-atoms in the ortho-position, "united by nine bonds," he calls an oiazine-derivative. The present substance is a derivative of dihydro-oiazine, but whether the formula I or II represents its constitution cannot in the meantime be decided. No. I (1, 3, 5, 6) seems the more probable.


Dihydro-oiazine.

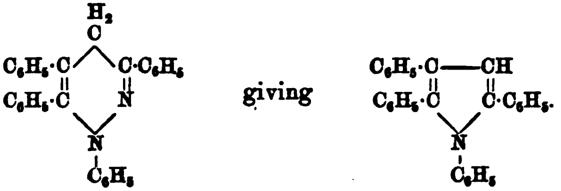

(1, 3, 5, 6) (1, 3, 4, 6)
Tetraphenyl dihydro-oiazine.

Tetraphenyldihydro-oiazine is soluble in boiling, but only slightly soluble in cold, alcohol. It is very soluble in hot glacial acetic acid; it is also soluble in ether and in benzene. It is not affected by hydrochloric acid or alkalis, even when heated. The crystals, when pure, do not decompose till heated above 230°.

Action of Excess of Phenylhydrazine on Tetraphenyldihydro-oiazine.

Tetraphenyldihydro-oiazine is, as has been shown, a tolerably stable substance. The decomposition, therefore, which it easily undergoes in presence of excess of phenylhydrazine is all the more interesting. Tetraphenylpyrroline, identical with that described above, seems to be the chief product. An atom of nitrogen is eliminated, and the excess of phenylhydrazine acts as an oxidising agent to the extent of removing one atom of hydrogen (just as it does in the case of phenylmethylpyrazolone, Knorr, *Annalen*, **238**, 168) from the remainder.

$$2C_{28}H_{22}N_2 + C_6H_5N_2H_3 = 2C_{28}H_{21}N + N_2 + NH_3 + C_6H_5{\cdot}NH_2.$$



If equal weights of desylacetophenone and phenylhydrazine be dissolved in glacial acetic acid, and the mixture, instead of being merely warmed, as in making the oiazine-derivative, be boiled for two hours, then, on cooling, nothing crystallises from the now dark, reddish-brown liquid. If before it cools, however, a little water be added, then it deposits tetraphenylpyrroline in an amorphous form. The quantity is extremely small, and as a large amount of tarry matter is formed at the same time, it was found extremely difficult to purify it. After several recrystallisations from alcohol, which, as it is somewhat soluble in cold alcohol, greatly diminished the quantity available for examination, it was still not perfectly pure. Its melting point was 192—194°, but not sharp, that of tetraphenylpyrroline being 196—197°; and a small portion, recrystallised once more from glacial acetic acid, melted at 196° sharply. It exactly resembled that substance in appearance, and gave the pyrroline reaction. The analysis of the specimen melting between 192° and 194°, although the substance was not yet quite pure, served to confirm the theory.

I. 0·2358 gram substance gave 0·7766 gram CO_2 and 0·1240 gram H_2O.

II. 0·2444 gram substance gave 0·8047 gram CO_2 and 0·1308 gram H_2O.

III. 0·2911 gram substance gave 10 c.c. nitrogen at 18° C. and 763 bar.

	Found.			Calculated for $C_{28}H_{21}N$.
	I.	II.	III.	
C	89·81	89·80	—	90·56
H	5·84	5·94	—	5·66
N	—	—	4·05	3·8

Action of Hydroxylamine on Desylacetophenone.

As is frequently the case with 1 : 4- diketones (see V. Meyer, *Berichte*, **21**, 1361), the action of hydroxylamine is not so simple as with ordinary ketones. Desylacetophenone seems to yield three different products melting respectively at 151°, 189°, and 215°. Of these, only the first and last, the mono- and di-hydroximes, could be prepared in sufficient quantities, and pure enough for examination.

The Monhydroxime, $C_{22}H_{18}O{:}NOH$.

One mol. of desylacetophenone, 3 mols. of hydroxylamine hydrochlorate, and 3 mols. of sodium hydrate or acetate are mixed with glacial acetic acid, the last two having been previously dissolved in a little water. The mixture, after being warmed gently on the water-bath till the whole has dissolved, soon begins to deposit sodium chloride, and in a few minutes some of the hydroxime also separates in larger crystals. The warming is now stopped, and the contents of the flask are decanted from the sodium chloride and allowed to cool, when a large quantity of the monhydroxime crystallises out. When recrystallised by dissolving in warm glacial acetic acid, and adding a little water, it melts at 151°. As is shown by the analysis, it appears to contain a small proportion of the dihydroxime, from which it could not be freed by recrystallisation. The only other possible assumption, that it is an internal anhydride, formed by the loss of an extra molecule of water, would also account for the excess of nitrogen, but this would demand, on the other hand, a higher percentage of carbon, whereas that found is smaller.

Analysis :—

I. 0·2374 gram substance gave 0·6943 gram CO_2 and 0·1261 gram H_2O.

II. 0·4665 gram substance gave 19 c.c. nitrogen at 17° and 758·5 mm. bar.

	Found.		Calculated.	
	I.	II.	Monoxime, $C_{22}H_{19}O_2N$.	do. $-H_2O$, $C_{22}H_{17}ON$.
C...........	79·76	—	80·24	84·88
H..........	5·90	—	5·77	5·46
N...........	—	4·79	4·25	4·5

It is soluble in ether and alcohol, very soluble in hot glacial acetic acid, insoluble in boiling water, and insoluble also in alkalis.

The Dihydroxime, $C_{22}H_{18}(NOH)_2$.

One mol. desylacetophenone is dissolved in alcohol, and 2½ mols. of hydroxylamine hydrochloride and 6 mols. of sodium hydrate, each dissolved in a little water, are added, and the whole boiled for four hours, using a reflux condenser. The alcohol is then partly distilled off, and the mixture poured into water. A copious, curdy precipitate, consisting to a large extent of the monohydroxime in a very impure condition, is at once produced. The liquid is filtered, and the filtrate acidified with hydrochloric acid. The precipitate which now appears is chiefly composed of the dihydroxime. It is collected on a filter, washed with alcohol, and dried. As it could not be purified by recrystallisation in the ordinary way, it was dissolved in glacial acetic acid, and a little water and alcohol were added to the hot solution. A white precipitate of irregularly formed crystals gradually separated.

It melts at 215° exactly, giving off bubbles of nitrogen. It is insoluble in alkalis, even when hot.

Analysis:—

0·1964 gram substance gave 13·8 c.c. nitrogen at 16° C. and 757 mm. bar.

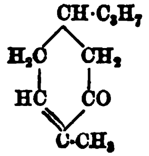
	Found.	Calculated for $C_{22}H_{20}O_2N_2$.
N	8·3	8·1

Further applications of potassium cyanide under conditions similar to the above are at present being investigated.

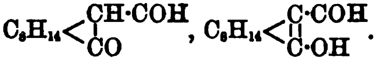
XLVI.—*Action of Ethyl Oxalate on Camphor.*

By J. Bishop Tingle, Ph.D.

It has been shown by Claisen and his pupils (*Berichte*, **20**, 655, 2078, 2188) that in the presence of sodium ethylate certain acid ethers combine with ketones with the production of ethyl salts of diketonic acids, $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}COOC_2H_5$. According to Claisen, the reaction probably takes place in two stages. An ortho-compound is first formed, thus:—$R{\cdot}CO{\cdot}OC_2H_5 + C_2H_5{\cdot}ONa = R{\cdot}C(ONa)(OC_2H_5)_2$. This then acts upon the ketone, alcohol being eliminated, $R{\cdot}C(ONa)(OC_2H_5)_2 + H_2CH{\cdot}CO{\cdot}R = R{\cdot}C(ONa){:}CH{\cdot}CO{\cdot}R + 2C_2H_5{\cdot}OH$. From this, on acidification, the symmetrical compound $R{\cdot}CO{\cdot}CH_2{\cdot}CO{\cdot}R$ is formed. This reaction has been proved to be a general one for ketones containing the groups $R{\cdot}CO{\cdot}CH_3$ or $R{\cdot}CO{\cdot}CH_2R$. W. Wislicenus (*Annalen*, **246**, 337, 339) has shown that the same applies to the ethyl salts of the fatty acids. Thus, ethyl oxalate and ethyl butyrate readily yield ethyl oxalobutyrate, but no corresponding compound with ethyl isobutyrate has been obtained. It has therefore been proposed to apply Claisen's reaction to ketones of unknown constitution in order to determine whether they contain a CH_3- or CH_2-group. Ordinary camphor must be regarded as a ketone, since it forms a hydroxime and a phenylhydrazone. Its constitution is usually expressed by the formula—

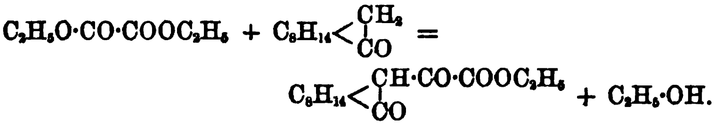


This was first proposed by Kekulé (*Berichte*, 6, 931), who, however, pointed out that the position of the double bond relative to the carbonyl oxygen and the two side chains was not conclusively proved. By the action of ethyl formate upon camphor in presence of metallic sodium, Bishop and Claisen (*Berichte*, 22, 533) obtained a compound of the composition $C_{11}H_{16}O_2$, which they regarded as having a constitution expressed by one or other of the following formulæ:—



$$C_8H_{14}<\begin{matrix}CH\cdot COH\\ |\\ CO\end{matrix}, \quad C_8H_{14}<\begin{matrix}C\cdot COH\\ \|\\ C\cdot OH\end{matrix}.$$

With the hope of being able to throw some light upon the properties of camphor, I recently undertook the study of its action upon ethyl oxalate. Being compelled, however for the present, to suspend my work in this direction, I wish to place on record the results of my experiments so far, reserving a fuller investigation for a later period. I have already shown ("Inaug. Diss.," Munich, 1889) that ethyl oxalate combines with sodium camphor in hot toluene solution, the yield of double ketone being, however, very small. Much better results have been obtained by the use of sodium wire in anhydrous ether. Under these conditions ethyl oxalate reacts with camphor according to the following equation:—

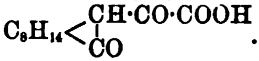


$$C_2H_5O\cdot CO\cdot COOC_2H_5 + C_8H_{14}<\begin{matrix}CH_2\\ |\\ CO\end{matrix} =$$
$$C_8H_{14}<\begin{matrix}CH\cdot CO\cdot COOC_2H_5\\ |\\ CO\end{matrix} + C_2H_5\cdot OH.$$

Ethyl camphor-oxalate is a thick, oily liquid, giving an intense dark-red coloration with ferric chloride. On distillation, even under reduced pressure, it undergoes decomposition, so that no constant boiling point can be observed. The yield is about 50 per cent. of the ethyl oxalate employed, but, in addition to this, a considerable quantity of camphor-oxalic acid may be obtained. Methyl oxalate gives a corresponding compound; this, like the ethyl compound, is a thick, viscid liquid, giving a ruby colour with ferric chloride solution. The sodium salts of these compounds are yellow solids, which easily undergo decomposition in the air.

Camphor-oxalic Acid.

Is obtained by treating ethyl camphor-oxalate with an excess of potassium hydrate solution in the cold for two to three days. The solution is acidified and extracted with ether, and, on evaporation of the ethereal solution, the acid crystallises out in the form of large, rhombic plates. The compound is best purified by recrystallisation from light petroleum; it melts at 88°, is sparingly soluble in water or alcohol, but readily dissolves in sodium carbonate solution, from which it is precipitated unchanged by hydrochloric acid. The analysis agrees with the formula



$$C_8H_{14}<\begin{array}{l}CH\cdot CO\cdot COOH\\ |\\ CO\end{array}.$$

0·2944 gram substance gave 0·1918 gram H_2O and 0·694 gram CO_2.

	Found.	Calculated for $C_{12}H_{16}O_4$.
C	64·29	64·28
H	7·24	7·14

The calcium, barium, and zinc salts of camphor-oxalic acid are obtained as amorphous precipitates on adding the respective chlorides to a neutral solution of the ammonium salt. The zinc salt is the least soluble, and the barium salt the most soluble, in water. The copper and silver salts are also amorphous, and sparingly soluble in water. The colour of the former is green, that of the latter slightly yellowish. The silver salt rapidly decomposes on exposure to air and light.

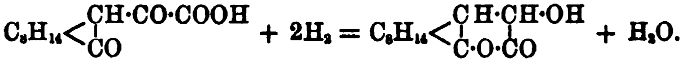
Reduction of Camphor-oxalic Acid.

On treating camphor-oxalic acid with excess of sodium amalgam (3 per cent. of sodium), acidifying the solution, extracting it with ether, and evaporating, an oily residue is obtained. This is purified by dissolving it in excess of warm solution of barium hydrate, passing carbon dioxide until no further precipitate is formed, filtering and acidifying the solution, and extracting it with ether. On evaporation of the ether, a white, amorphous solid remains, which melts at 75—76°, is very soluble in benzene, and somewhat greasy to the touch. The following results were obtained on analysis:—

0·2864 gram substance gave 0·7188 gram CO_2 and 0·2224 gram H_2O.

	Found p. c.	Calculated for $C_{12}H_{18}O_3$.
C	68·45	68·57
H	8·63	8·57

From its properties and the manner in which it is obtained, this compound is a lactone; its mode of formation and constitution are shown by the equation—



$$C_8H_{14}<\begin{array}{l}CH\cdot CO\cdot COOH\\ |\\ CO\end{array} + 2H_2 = C_8H_{14}<\begin{array}{l}CH\cdot CH\cdot OH\\ |\qquad\ \ |\\ C\cdot O\cdot CO\end{array} + H_2O.$$

Monophenylhydrazone Ethyl Camphor-oxalate.

A slight excess of phenylhydrazine is added to an ethereal solution of ethyl camphor-oxalate, and the mixture boiled for about three hours. The crystals obtained on cooling the solution are washed with ether and recrystallised twice from toluene. When pure, the hydrazone consists of fine, white, needle-shaped crystals melting at 187—188° with evolution of gas. The compound is slightly soluble in alcohol and benzene, and insoluble in potassium hydrate solution; it gives a deep-blue coloration with nitric acid. Analysis:—

0·2069 gram substance gave 0·5286 gram CO_2 and 0·1443 gram H_2O.

0·2064 gram substance gave 15·575 c.c. nitrogen at 7·5° C. and 726 mm. pressure.

	Found.	Calculated for $C_{20}H_{26}O_3N_2$.
C................	69·98	70·17
H	7·77	7·60
N	8·61	8·19

Ethyl Camphor-oxalate and Hydroxylamine.

If ethyl camphor-oxalate is heated on the water-bath for about six hours with a large excess of hydroxylamine, a considerable quantity of a white substance is formed which crystallises in silky needles melting at 193° with decomposition. The compound is very insoluble in water, but soluble in benzene, from which it is deposited in a gelatinous condition on cooling. It may be recrystallised from dilute alcohol. In spite of its constant melting point, the substance was probably impure, as no definite results were obtained on analysis. I propose to examine this compound more fully at a later period, as well as the derivatives formed by the action of ammonia.

Ethyl Camphor-oxalate and Aniline.

Ethyl camphor-oxalate and aniline appear to react in the cold, though only to a slight extent. On heating to 165° for some time, a considerable quantity of crystals were obtained which, after purification, melted at 241°. This compound proved to be oxanilide; its formation is an additional support to the formula already given to ethyl camphor-oxalate.

XLVII.—*On the Molecular Weights of Metals when in Solution.*

By C. T. Heycock, M.A., and F. H. Neville.

Part II.

Section C.—Thermometry.

The experiments described in the previous paper, this vol., p. 393, were all made with mercurial thermometers. As the method by which the fixed points, on our thermometers, were determined to a great extent eliminates the necessity for the very doubtful correction of the portion of column immersed and unimmersed, we think it may be of interest to chemists generally. The mercury thermometers were made for us by Mr. Hicks, of Hatton Garden, to whom we are much indebted for the great care taken in their manufacture. These thermometers were 15 in number, and covered a range from 0° C. to 325° C.; they were graduated in millimeters, and had an expansion chamber just above the bulb, and a safety chamber at the top of the stem. Each thermometer covers a range of 28°, and overlaps the one below it by about 4°, the length of the stem being about 2 feet. Each millimeter corresponded to about 0·05°, and as the readings were always taken with a telescope and cross-wires, a fifth of this quantity, or 0·01°, could be read with considerable ease and certainty. The "zero" of each thermometer had been fixed by the method patented by Mr. Hicks, of heating them for a fortnight in boiling oil. For temperatures below 250°, this fixing of the zero is nearly perfect. Thus thermometer No. 10 (range from 210—237°), with which most of the experiments described in this paper were made, gave the following values for the freezing point of tin:—

August 8th, 1889	5389·5 mm.
March 1st, 1890	5393·0 „

showing a total rise of 3·5 mm. = 0·17°.

Between these dates the thermometer was used for several hundred experiments, and was kept nearly daily for two months continuously plunged in molten tin for seven or eight hours, a treatment which will be admitted was somewhat severe. It is worthy of note that this slight rise of 3·5 mm. was quite gradual.

The calibration of the thermometers 8, 9, 10 was effected by the step-by-step method, and curves were afterwards plotted, so that the temperatures Centigrade corresponding to the millimeter divisions could be read off at once. Threads of mercury of suitable length for calibration were separated by the method recommended in the Report of the British Association Committee on Thermometry for the Southampton Meeting in 1882. This method consists in running mercury from the bulb into the stem, and then heating the stem with a small flame about the size of a hemp seed; the mercury boiling at this point separates the thread. By this means, threads of almost any desired length can be easily obtained, although at first it requires a certain amount of courage to heat the fairly thick stem of a good thermometer, especially where the lines are engraved upon it. We fortunately, however, met with no accident in several trials.

The fixed points on the thermometers supplied to us by Mr. Hicks were determined with the stem completely immersed, and as the correction for the immersed and unimmersed portion of the column is by all admitted to be subject to very considerable errors, it became necessary, in order to get observations which should be continuous from one thermometer to another, to redetermine the fixed points under the same conditions as those in which they were to be used. For this purpose, we used a platinum thermometer,* which was a much modified form of the thermometer used by Callendar (*Phil. Trans.*, 1887) in his comparison of the air and platinum thermometers.

Three of these platinum thermometers, called A, B, and C, were constructed in the following way:—A piece of quill tubing, about a foot in length, had a slightly larger tube welded to it; down the axis of the tube passed a still finer tube, in which were several strands of stout silver wire, whilst in the annular space between the two tubes more strands of silver were passed; these silver wires were fastened at the top to stout binding screws insulated on ebonite, whilst the bottom of the wires were soldered to the two ends of a thin platinum wire 2 or 3 feet in length. This platinum wire was covered with pieces of capillary glass tube, each about an inch long, the ends of the glass tubes being about ⅛th of an inch apart from each other. The wire was then folded **W**-wise, the limbs of the **W** being insulated from each other, whilst the top and bottom of the arms were formed by the uncovered portions of the wire.

After folding, this insulated wire was tucked into the larger glass tube, round the central axial tube, forming a single layer around it. The larger tube was then sealed off, and the thermometer was complete.* In size the "bulb" was almost exactly the same diameter as the mercury thermometer we have described, and of about the same length.

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* We must here express our best thanks to our friend Mr. E. H. Griffiths, of Sidney College, for devising and making a special form of platinum thermometer, and for determining its fixed points. The confidence we feel in giving actual temperatures, instead of mere differences, is entirely owing to the great care he took in the determinations.

The resistances were determined by means of a large box specially constructed by Messrs. Elliott, the reduction values for each coil in the box having been determined for changes in temperature. The temperature of the coils was afterwards kept almost stationary at 16° by means of a copper water-bath holding four or five gallons, the temperature of which was controlled by a gas regulator.

The galvanometer had a resistance of about 8,000 ohms; hence the thermoelectric effects were rendered unimportant.

One Leclanché cell was used to furnish the current, as it was found that with two or three cells an appreciable increase of resistance could be observed owing to the heating of the wire.

Determination of Fixed Points on the Platinum Thermometers.

The zero point was determined by leaving the thermometers in thoroughly washed ice, using the precautions mentioned by Guillaume ("Traité pratique de la thermométrie de précision," 1889).

The boiling point of water was determined in a large copper hypsometer of the usual form, provided with a manometer.

The remaining boiling points were all determined in fractionating round-bottomed glass vessels with long necks. For sulphur, aniline, naphthalene, and mercury, these flasks have a capacity of nearly 2 litres; for the other substances rather smaller flasks were used.

The bulb of the thermometer when the distillation commenced was always somewhat above the surface of the liquid. The mouth of the flask was generally closed with cotton wool or asbestos cloth.

At first great difficulty, even with these large flasks, was experienced from superheating, especially in the case of the monatomic mercury vapour. We think that we finally overcame this difficulty by setting the boiling flask on a plate of asbestos card-board about 18 inches square, in the centre of which a circular hole was cut so that the flame of the lamp only played on a few inches of the bottom of the flask, the surface of the liquid being always well above the asbestos. The upper part of the flask was wrapped in asbestos cloth. In consequence of these precautions, the temperature was proved to be independent of the size of the flame used for heating.

---

* Since these thermometers were made, Mr. Griffiths has made others entirely with platinum wires, to avoid thermoelectric effects. An account of these new thermometers was read before the Royal Society on June 19th, 1890, as part of a paper on the determination of some melting points by E. H. Griffiths, M.A.

The substances used were the purest that could be obtained from Messrs. Hopkin and Williams, and Harringtons, and Kaulbaum.

The naphthalene, aniline, and benzophenone were distilled between 20 and 30 times; not only were the final boiling points the same as the earlier ones, but these substances were individually fractionated in the natural course of each experiment without producing the slightest change.

We were not able, however, to attach the same value to methyl salicylate that Professor Ramsay does, as it generally showed a slight rise during the experiments, probably owing to saponification from traces of water vapour. About three-fourths of a litre of aniline, liquid naphthalene, and sulphur were used in each experiment, and about 300 c.c. of redistilled mercury.

The quantities of benzophenone and methyl salicylate were smaller, but the same precautions to avoid superheating were used.

In the case of water, mercury, and sulphur, there was no difficulty in reducing the temperatures of the boiling point to the standard pressure of 760 by the aid of Regnault's tables. In the case of naphthalene and benzophenone, we used the formulæ given by Guillaume (*loc. cit.*. p. 272), deduced from Craft's values (*Bull. Soc. Chim.*, 1883, **39**, 277).

That is, for naphthalene, $$\text{b. p.} = 218{\cdot}06 + \frac{\text{H} - 760}{17{\cdot}1},$$

" benzophenone, $$\text{b. p.} = 306{\cdot}08 + \frac{\text{H} - 760}{15{\cdot}8}.$$

Crafts, p. 231 of the *Bull. Soc. Chim.*, points out that the advantages of benzophenene and naphthalene are that whilst their melting points can be readily determined, impurities affect the melting point of these substances much more than the boiling point. We determined the melting points of these bodies as used by us by means of a thermometer constructed by Geissler and graduated in fifths, and found—

M. p. benzophenone,		47·8—47·9, before being used.
"	"	47·8, after all the determinations had been made.
"	naphthalene	79·7, before being used.
"	"	79·6, after using.

Crafts gives as the true values for $C_{10}H_8$, 79·6—79·9°; and for $C_6H_5{\cdot}COC_6H_5$, 47·7—48°; hence it will be seen that our samples were perfectly pure.

Having determined the resistances of the platinum thermometers for the above five points, a curve was constructed to enable us to determine intermediate temperatures. We followed the very convenient plan adopted by Callendar. This consists in first calculating the quantity $\frac{R_t - R_0}{R_{100} - R_0} \times 100$, and calling this the Pt temperature. In this formula R_t = observed resistance at Centigrade temperature t, R_0 and R_{100} being resistance in ice and steam respectively. If the resistance change of a wire was directly proportional to the change of temperature, this formula would give the temperature at once.

This Callendar calls the platinum temperature, which, for convenience, may be called Pt. For temperatures above 100°, Pt was considerably less than the temperature given by the air thermometer, as the following table will show for the thermometer A:—

	Resis. of coil in ohms.	Pt temp.	Temp. C.°	Temp. C. − temp. Pt, called D.
Ice	14·068	0	0	0
Steam	18·601	100	100	0
Naphthalene, b. p.........	23·720	212·88	218·06	5·18
Benzophenone, b. p.......	27·389	293·81	306·08	12·27
Sulphur, b.p.............	32·915	415·68	448·38	32·70

Each of the Pt temperatures in the above table is the mean of a great number of concordant experiments taken on different days.

Then, following Callendar's method, a curve was plotted, having Pt for abscissa and D for ordinate, and passing through the five points given by the above table. The scale that had to be adopted to read to $\frac{1}{100}$° C. is too large to be reproduced. But an equation of the form $y = ax + bx^2 + cx^3 + dx^4$ was assumed, the constants determined, and the curve used to determine the b. p. of aniline, methyl salicylate, and mercury, and the results were found to be identical with those given by the chart.

In order to check the trustworthiness of these thermometers, we have used the experiments on the boiling points of aniline, methyl salicylate, and mercury. Although in determinations of our thermometers, the platinum thermometer A alone was used, we give some results of boiling points with B and C as determined from their curves, and include in the same table the standard boiling points.

Aniline.			Methyl salicylate.			Mercury.		
A.	B.	C.	A.	B.	C.	A.	B.	C.
184·32	184·27	184·29	223·08	223·12	223·16	357·61	357·59	357·65
184·29			223·12			357·62		

Aniline................	183·7	Thorpe.[*]
„	184·4	Ramsay.
Methyl salicylate.......	222·9	Ramsay.
Mercury	357·25	Regnault.
„	358·2	Ramsay.

It will be seen that the numbers given by the platinum thermometer lie in each case between the values given by the above-named observers.

We felt justified from this in concluding that the platinum thermometer A could be used with confidence for determining temperatures up to the boiling point of sulphur with a probability of a very small error, and that for the particular purpose which we needed, that is, that of determining the *range of temperature* of a thermometer covering only about 25°, the error would be exceedingly small. In other words, that the value of each mm. of our mercury thermometer scales would be satisfactorily determined.

Comparison of the Mercury with the Platinum Thermometers.

For the purpose of comparison, the mercury thermometers were placed alongside the platinum thermometer and immersed to the usual depth in the axis of one of the iron blocks in a bath of melted metal kept stirred, as before described for tin. The fixed points were thus determined under exactly the working conditions, and the error on account of the unimmersed part of the mercury was practically eliminated, except for the slight variations of temperature of the room. In thermometers in which so small a fraction of the total weight of the mercury is in the stem, this slight change of temperature may be neglected. The fixed points once determined, care was taken to calibrate the thermometer by the step-by-step method, and careful charts of the bores were made.

In spite of the precautions, we think now, however, that greater accuracy might be obtained by means of the platinum thermometers, although we believe that the accuracy of our results is sufficiently great to give confidence in the table of atomic falls.

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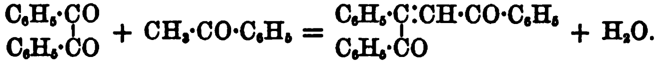
[*] There is some doubt as to the conditions under which this point was determined by Thorpe.

XLVIII.—*αβ-Dibenzoylcinnamene and the Constitution of Zinin's Lepiden and its Derivatives.*

By FRANCIS R. JAPP, F.R.S., and FELIX KLINGEMANN, Ph.D.

αβ-Dibenzoylcinnamene (anhydracetophenonebenzil) was obtained by Japp and Miller (Trans., 1885, 35) by the condensation of benzil with acetophenone under the influence of caustic potash:—



$$\begin{array}{l} C_6H_5\cdot CO \\ | \\ C_6H_5\cdot CO \end{array} + CH_3\cdot CO\cdot C_6H_5 = \begin{array}{l} C_6H_5\cdot C{:}CH\cdot CO\cdot C_6H_5 \\ | \\ C_6H_5\cdot CO \end{array} + H_2O.$$

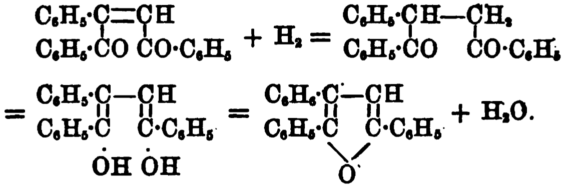
The reactions of this compound with hydriodic acid, with hydrochloric acid, and with phenylhydrazine have been partly studied, without, however, any conclusion being arrived at as to the constitution of the compounds formed (Japp and Burton, Trans., 1887, 430; Japp and Huntly, *ibid.*, 1888, 184).

The important results obtained by Paal and others in investigating the reactions of saturated γ-diketones suggested to us that a study of an unsaturated γ-diketone—to which class dibenzoylcinnamene belongs—might yield results of interest, and we were the more induced to attack this problem by the fact that, by a slight modification of the method employed by Japp and Miller, dibenzoylcinnamene can be readily prepared in any desired quantity.

Our work has thrown unexpected light on the constitution of Zinin's lepiden and its derivatives. As we regard this as its most important outcome, we shall arrange our results so as to exhibit their relation to those obtained by Zinin. Many of the reactions here described were suggested by the analogy of Zinin's work.

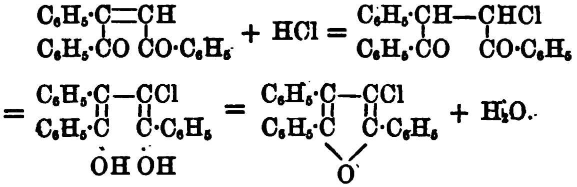
PART I. THEORETICAL.

In a preliminary note (*Ber.*, **21**, 2933), we pointed out that the compounds $C_{22}H_{16}O$ and $C_{22}H_{15}ClO$, obtained by the action of hydriodic acid and hydrochloric acid on *αβ*-dibenzoylcinnamene (Trans., 1887, 430), might be regarded as furfuran-derivatives—namely, as *triphenylfurfuran* and *triphenylchlorofurfuran*. In the formation of the first of these, the final result of the reaction is the removal of an atom of oxygen from dibenzoylcinnamene. It is probable, however, that under the reducing influence of the hydriodic acid a saturated γ-diketone is first formed, which then changes into the tautomeric form, and finally parts with water, as in the well-known reactions described by Paal:—



Triphenylfurfuran.

In the reaction with hydrochloric acid the formation of an intermediate additive compound is also assumed:—

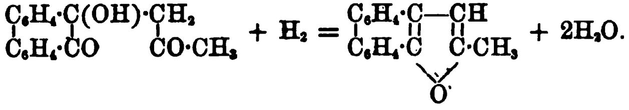


Triphenylchlorofurfuran.

The chlorine-atom in this compound is very firmly attached; but by heating the substance in alcoholic solution with sodium amalgam for several days, we succeeded in converting it into the foregoing triphenylfurfuran.

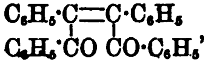
By the action of sodium and boiling amyl alcohol on triphenylfurfuran an oil was obtained, which was probably a tetrahydro-compound, $C_{22}H_{20}O$. The analytical figures would, however, also agree with the composition of a hexahydro-compound.

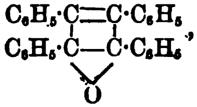
The compound $C_{17}H_{12}O$, obtained by Japp and Miller by the reduction of acetonephenanthraquinone with zinc-dust and acetic acid (Trans., 1885, 18), may, as we pointed out, be regarded as *diphenylenemethylfurfuran*. Omitting the intermediate stage, which, as in the foregoing cases, would consist in the formation of a saturated γ-diketone, the reaction may be expressed as follows:—



Diphenylenemethylfurfuran.

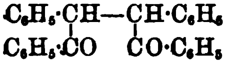
The foregoing method gives a very poor yield; but we find that when acetonephenanthraquinone is warmed for a few minutes with fuming hydriodic acid, it is converted almost quantitatively into *diphenylenemethylfurfuran.* The better yield thus obtained enabled us to purify the compound thoroughly, and the melting point was found at 123—124°, instead of at 121° as given by Japp and Miller.

An attempt to prepare dibenzoylstilbene,  $\begin{array}{l} C_6H_5\cdot C{=}C\cdot C_6H_5 \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array}$, in order to convert it by the action of hydriodic acid into tetraphenylfurfuran failed; but we pointed out (*Ber.*, **21**, 2934, foot-note) that possibly Zinin's lepiden, $C_{28}H_{20}O$, melting at 175° (*Beilstein's Handbuch*, 2nd ed., **3**, 112) was the desired tetraphenylfurfuran. In making this suggestion, it had escaped our notice that a similar idea had been put forward by Dorn as early as 1870 (*Annalen*, **153**, 358). Dorn calls lepiden "oxyphenyltetrol," and ascribes to it the formula



which would represent it as a tetraphenylfurfuran with the furfuran nucleus proposed by H. Schiff in 1877 (*Ber.*, **10**, 1193).

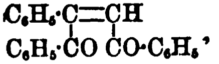
Magnanini and Angeli (*Ber.*, **22**, 853) have since found that Zinin's hydro-oxylepiden is identical with Knoevagel's bidesyl,



$$\begin{array}{l} C_6H_5\cdot CH{-}CH\cdot C_6H_5 \\ C_6H_5\cdot CO\ \ \ CO\cdot C_6H_5 \end{array}$$

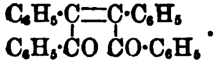
(*Ber.*, **21**, 1355); and by the dehydrating action of hydrochloric acid they have converted bidesyl into tetraphenylfurfuran, identical with lepiden. They regard Zinin's oxylepiden, $C_{28}H_{20}O_2$ (m.p. 220°), as having the formula of the before-mentioned dibenzoylstilbene, which we failed in preparing.

Magnanini and Angeli's view would make oxylepiden a strict analogue of $\alpha\beta$-dibenzoylcinnamene: oxylepiden would be phenyldibenzoylcinnamene:—



$$\begin{array}{l} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array},$$

$\alpha\beta$-Dibenzoylcinnamene.



$$\begin{array}{l} C_6H_5\cdot C{=}C\cdot C_6H_5 \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array}.$$

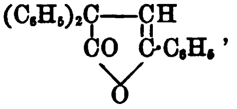
Dibenzoylstilbene
(Oxylepiden, m. p. 220°).

In support of this view, we find that there is an almost perfect parallelism in behaviour between dibenzoylcinnamene and oxylepiden. The various compounds which we have obtained from dibenzoylcinnamene stand to the corresponding compounds of the lepiden series in the relation of triphenyl-derivatives to tetraphenyl-derivatives, a relation which is exhibited, in the first place, in the case of dibenzoylcinnamene and oxylepiden themselves. It is necessary, however, to point out that, of the three "oxylepidens" prepared by Zinin, the analogue of dibenzoylcinnamene is "acicular oxylepiden" (m. p. 220°).

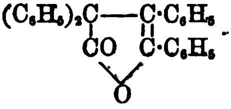
By heating "acicular oxylepiden" with hydriodic acid, Berlin (*Annalen*, **153**, 131) converted it into lepiden (tetraphenylfurfuran). As already mentioned, we have shown that dibenzoylcinnamene, when subjected to the same treatment, yields triphenylfurfuran.

Zinin has shown (*Beilstein's Handbuch*, 2nd ed., 3, 113) that by treatment with nitric acid lepiden is oxidised to "acicular oxylepiden." We find that by the same treatment triphenylfurfuran yields *αβ*-dibenzoylcinnamene, which is, however, converted in the process into its mononitro-derivative.

By heating "acicular oxylepiden," Zinin obtained two isomeric "oxylepidens:" as chief product "tabular oxylepiden" (m. p. 136°), and in small quantity "octahedral oxylepiden" (m. p. 232°) (*Beilstein's Handbuch, loc. cit.*). In like manner, by heating dibenzoylcinnamene, we have succeeded in converting it into two isomerides: a compound formed in large quantity, melting at 117—118°, corresponding with "tabular oxylepiden;" and a compound formed only in very small quantity, melting at 197—198°, corresponding with "octahedral oxylepiden." We regard the compound melting at 117—118° as *triphenylcrotolactone*, and "tabular oxylepiden" as *tetraphenylcrotolactone*:—



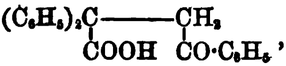
Triphenylcrotolactone (m. p. 117—118°).



Tetraphenylcrotolactone ("tabular oxylepiden").

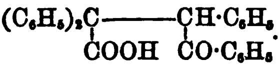
By oxidation with excess of chromic anhydride, triphenylcrotolactone yields benzophenone and benzoic acid. Zinin does not appear to have oxidised "tabular oxylepiden," but he obtained benzophenone by the oxidation of the so-called isolepiden (*v. infra*) which is formed from "tabular oxylepiden" by distillation.

Caustic potash in alcoholic solution converts triphenylcrotolactone into a salt of *α-diphenyl-β-benzoylpropionic acid.* Zinin has shown that "tabular oxylepidene" yields, by the same treatment, oxylepidenic acid, $C_{28}H_{22}O_3$. We assign to these acids the following formulæ:—



$$\begin{array}{ll}(C_6H_5)_2\underset{|}{C}\text{———} & \underset{|}{C}H_2 \\ \quad COOH & CO\cdot C_6H_5 \end{array},$$

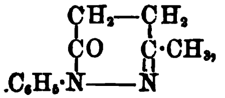
α-Diphenyl-*β*-benzoylpropionic acid (m. p. 182—183°).



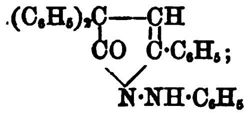
$$\begin{array}{ll}(C_6H_5)_2\underset{|}{C}\text{———} & \underset{|}{C}H\cdot C_6H_5 \\ \quad COOH & CO\cdot C_6H_5 \end{array}$$

Oxylepidenic acid.

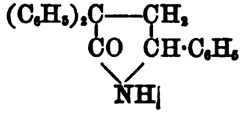
Diphenylbenzoylpropionic acid displays the behaviour of lævulic acid and other γ-ketonic acids. Thus, when heated with phenylhydrazine at 150°, it reacts, eliminating *two* mols. of water, and yielding the compound $C_{28}H_{22}N_2O$ (m. p. 185°), which would correspond with the anhydride of phenylhydrazonelævulic acid. E. Fischer, however (*Annalen*, **236**, 148), assigns to the latter compound the formula—



whereas the behaviour of the compound from diphenylbenzoylpropionic acid is better accounted for by the formula



thus, when reduced with sodium in boiling amyl-alcoholic solution, it eliminates the anilido-group, yielding 3-*diphenyl*-5-*phenylpyrrholidone*,



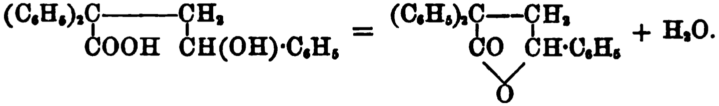
(m. p. 201°), the constitution of which will be proved later on by its preparation by a different method (*v. infra*).

Racine has shown (*Annalen*, **239**, 86) that phthalaldehydic acid, when treated with phenylhydrazine, parts with 2 mols. of water, yielding a compound $C_{14}H_{10}N_2O$; but when this compound is reduced (with tin and hydrochloric acid), it eliminates, not the anilido-group, but ammonia, forming phenylphthalimidine, $C_{14}H_{11}NO$.

It is evident, therefore, that there is more than one way in which acids containing a carbonyl-group in the γ-position to carboxyl can react with 1 mol. of phenylhydrazine eliminating 2 mols. of water; and the question of constitution can only be settled by the study of each compound separately. It is to be noted, however, that phthalaldehydic acid is not strictly comparable with diphenylbenzoylpropionic acid, as it cannot form a hydroxylated labile modification, from which alone a phenylhydrazine-derivative of the foregoing anilido-pyrrholone constitution could be derived. Lævulic acid, on the other hand, is in this respect analogous to diphenylbenzoylpropionic acid; but, nevertheless, Fischer's formula for the anhydride of phenylhydrazonelævulic acid must be accepted, as it is independently confirmed by work published later by Ach (*Annalen*, **253**, 44).

Diphenylbenzoylpropionic acid reacts with hydroxylamine hydrochloride at 100°, eliminating *two* mols. of water, and yielding a compound of the formula $C_{22}H_{17}NO_2$—a reaction which recalls that of benzallævulic acid with hydroxylamine described by H. Erdmann (*Annalen*, **254**, 184). If, on the other hand, diphenylbenzoylpropionic acid is heated with an excess of hydroxylamine hydrochloride at 150°, a process of deoxidation accompanies the introduction of the hydroxylamine residue, and a compound $C_{22}H_{17}NO$ is formed, isomeric with 3-diphenyl-5-phenylpyrrholone (*v. infra*). The constitution of these compounds has yet to be ascertained.

Sodium amalgam reduces diphenylbenzoylpropionic acid to a salt of *triphenyl-γ-hydroxybutyric acid*. This acid, when liberated from its salts, speedily parts with water, yielding *triphenylbutyrolactone* (m. p. 156°):—



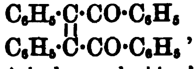
$$\begin{array}{ll}(C_6H_5)_2C & \!\!\!\text{———}CH_2 \\ \quad\; | & \quad\;\; | \\ \quad COOH & CH(OH)\cdot C_6H_5\end{array} = \begin{array}{ll}(C_6H_5)_2C & \!\!\!\text{—}CH_2 \\ \quad\; | & \;\; | \\ \quad CO & CH\cdot C_6H_5 \\ \multicolumn{2}{c}{\diagdown\!\diagup} \\ \multicolumn{2}{c}{O}\end{array} + H_2O.$$

This lactone may also be obtained directly from triphenylcrotolactone by boiling it with hydriodic acid.

When heated above its melting point, diphenylbenzoylpropionic acid is reconverted with loss of water into triphenylcrotolactone, a process which corresponds with the formation of the anhydrides of lævulic acid described by Wolff (*Annalen*, **229**, 249). Zinin has shown that oxylepidenic acid can be reconverted by the dehydrating action of heat into "tabular oxylepiden."

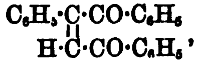
Zinin's "octahedral oxylepiden" and the corresponding compound melting at 197—198°, obtained from dibenzoylcinnamene, are difficult to prepare in quantity. The latter compound, in particular, has been only very cursorily examined. We incline to the view that these compounds are stereometric isomerides of "acicular oxylepiden" and αβ-dibenzoylcinnamene respectively, and would classify them as follows:—

Maleoïd form.



$$\begin{array}{l}C_6H_5\cdot C\cdot CO\cdot C_6H_5 \\ \quad\;\;\, \| \\ C_6H_5\cdot C\cdot CO\cdot C_6H_5\end{array},$$

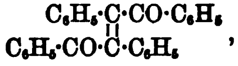
"Acicular oxylepiden" (m. p. 220°).



$$\begin{array}{l}C_6H_5\cdot C\cdot CO\cdot C_6H_5 \\ \quad\;\;\, \| \\ \quad H\cdot C\cdot CO\cdot C_6H_5\end{array},$$

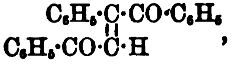
αβ-Dibenzoylcinnamene (m. p. 129°).

Fumaroïd form.



$$\begin{array}{r}C_6H_5\cdot C\cdot CO\cdot C_6H_5 \\ \| \qquad\qquad\quad \\ C_6H_5\cdot CO\cdot C\cdot C_6H_5 \qquad\end{array},$$

"Octahedral oxylepiden" (m. p. 232°).

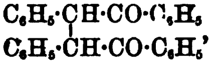


$$\begin{array}{r}C_6H_5\cdot C\cdot CO\cdot C_6H_5 \\ \| \qquad\qquad\quad \\ C_6H_5\cdot CO\cdot C\cdot H \qquad\qquad\end{array},$$

Iso-αβ-dibenzoylcinnamene (m. p. 197—198°).

The maleoïd constitution has in each case been assigned to the compound which has the lower melting point and the greater solubility, and which is converted by protracted heating into the isomeride of higher melting point and more sparing solubility.

Zinin also converts "acicular oxylepiden" into "octahedral oxylepiden" by heating it with caustic alkalis. This corresponds with the conversion of the maleoïd coumarinic acid into the fumaroïd orthocoumaric acid by the same treatment. This method cannot be employed in preparing isodibenzoylcinnamene, as dibenzoylcinnamene is resinised by heating with alkalis; but when dibenzoylcinnamene is heated with some of the primary alkylamines, a portion of it is converted into the iso-compound, the greater part, however, yielding nitrogenous derivatives (*v. infra*). This conversion takes place at a much lower temperature than when dibenzoylcinnamene is heated alone.

Again, it is characteristic of isomerism of the maleïc-fumaric type that both modifications yield on reduction the same saturated compound. Zinin has shown that both "acicular oxylepiden" and "octahedral oxylepiden" unite with nascent hydrogen to form the same hydro-oxylepiden (bidesyl),  $\begin{array}{l} C_6H_5\cdot CH\cdot CO\cdot C_6H_5 \\ \quad\quad\;\; | \\ C_6H_5\cdot CH\cdot CO\cdot C_6H_5 \end{array}$, which by dehydration is converted into tetraphenylfurfuran. We have not been able to obtain isodibenzoylcinnamene in sufficient quantity to study its behaviour towards reducing agents—to ascertain, for example, whether on boiling with hydriodic acid it is converted, like dibenzoylcinnamene, into triphenylfurfuran. The foregoing constitution is therefore assigned to it solely on the strength of its analogy in mode of formation and general physical properties to "octahedral oxylepiden."

By distilling "acicular oxylepidene" (the other two oxylepidens yield the same product), Zinin obtained from it a compound which he called *isolepiden* (m. p. 150°), assigning to it the formula $C_{28}H_{20}O$, whilst from the mother liquors from this substance he obtained by the action of caustic potash an acid of the formula $C_{28}H_{22}O_3$, to which he gave the name *isoxylepidenic acid*. Following this analogy, we distilled dibenzoylcinnamene, expecting to obtain from it isomerides of triphenylfurfuran and diphenylbenzoylpropionic acid respectively, but found that dibenzoylcinnamene was converted, with evolution of carbon monoxide, into a compound of the formula $C_{21}H_{16}O$ (m. p. 92—93°):—

$$C_{22}H_{16}O_2 = C_{21}H_{16}O + CO;$$

whilst by the action of potash on the mother liquors from this compound only ordinary diphenylbenzoylpropionic acid was obtained.

As these results were in contradiction to the strict analogy elsewhere observable in the two sets of compounds, we repeated Zinin's experiment on the distillation of oxylepiden, and found that the so-called isolepiden is formed, not by a process of deoxidation, as represented by Zinin, but with elimination of carbon monoxide:—

$$C_{28}H_{20}O_2 = C_{27}H_{20}O + CO,$$

So-called isolepiden.

and is, therefore, not an isomeride of lepiden at all. The formulæ of the various hydro-"isolepidens" and oxy-"isolepidens" described by Zinin must also, therefore, be correspondingly modified, thus:—

Dihydro-"isolepiden"................ $C_{27}H_{22}O$
Tetrahydro-"isolepiden".............. $C_{27}H_{24}O$
Oxy-"isolepiden" (3 isomerides)....... $C_{27}H_{20}O_2$.

From the mother liquors from the compound $C_{27}H_{20}O$, we obtained the so-called "isoxylepidenic acid," which proved, however, to be not isomeric, as stated by Zinin, but identical with oxylepidenic acid. The "acicular oxylepiden" is converted, during the heating, into "tabular oxylepiden," the greater part of which parts with carbon monoxide, forming "isolepiden," but a small portion distils unchanged and is hydrolysed in the subsequent treatment with alkali, yielding oxylepidenic acid.

The analogy between *αβ*-dibenzoylcinnamene and "acicular oxylepiden" is therefore preserved also in this case.

The remaining reactions of dibenzoylcinnamene described in this paper have not been studied by Zinin in the lepiden-series.

By acting on dibenzoylcinnamene with ammonia, we obtained (*Ber.*, **21**, 2936) two compounds of the formula $C_{22}H_{17}NO$, formed according to the equation:—

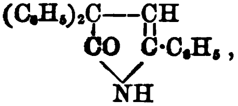
$$C_{22}H_{16}O_2 + NH_3 = C_{22}H_{17}NO + H_2O.$$

The first of these, melting at 180°, is prepared by mixing a warm alcoholic solution of dibenzoylcinnamene with alcoholic ammonia; the second, melting at 221°, is formed from the first by long boiling of its solutions, or by heating it alone to a temperature above its melting point.

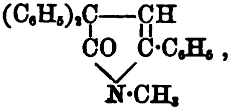
Primary alkylamines also react with dibenzoylcinnamene with elimination of water: thus, in the case of methylamine,

$$C_{22}H_{16}O_2 + CH_3{\cdot}NH_2 = C_{22}H_{16}(CH_3)NO;$$

but only one compound is formed in this case, although, owing to the fact that these alkylamine-derivatives exhibit dimorphism, we were, at first, disposed to assume the existence of isomerides. This methylamine-derivative, which melts at 138° or 143°, according to the crystalline form, corresponds with the ammonia-derivative melting at 221°. The constitution of these two compounds, as we shall show presently, may be represented by the formulæ



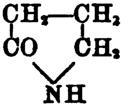
Ammonia-derivative
(m. p. 221°).



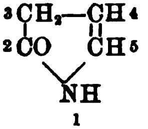
Methylamine-derivative
(m. ps. 138° *and* 143°).

leaving out of consideration the possibility that the ammonia-derivative may be a lactim, instead of, as here represented, a lactam. We have been unable to decide this latter point, as an attempt to methylate the ammonia-derivative gave no result.

We propose to adopt for these compounds a nomenclature based on that suggested by Tafel (*Ber.*, **22**, 1861). Tafel calls the saturated ring



*pyrrholidone.** In like manner, we term the unsaturated ring



pyrroholone—"pyrrholone" being equivalent to "ketopyrrholine," using "pyrrholine" in the generally accepted sense of "dihydropyrrhole."† The position of the substituting groups is indicated, following Tafel's practice, by the numerals attached to the foregoing formula, beginning with the imido-group, and counting towards the carbonyl-group. Thus the ammonia-derivative (m. p. 221°) would be 3-*diphenyl*-5-*phenylpyrrholone*, and the methylamine-derivative 1-*methyl*-3-*diphenyl*-5-*phenylpyrrholone.*

The constitution of these compounds is proved by the fact that they can be obtained by the action of ammonia and methylamine respectively on triphenylcrotolactone. Thus, in the case of the ammonia compound,

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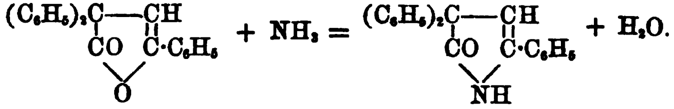
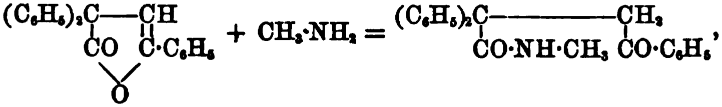
* Pyrrholidone itself has since been prepared by Gabriel (*Ber.*, **23**, 3338).

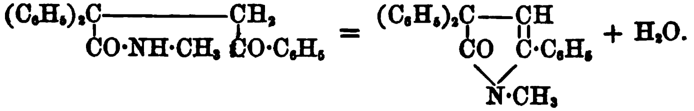
† In this paper "pyrrhole" is used as synonymous with "pyrroline" or "pyrrol."



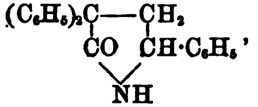
With methylamine, the reaction takes place in two stages. In the first of these, the methylamide of diphenylbenzoylpropionic acid is formed:—



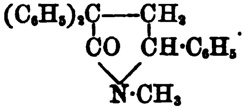
which, on heating, parts with water, yielding 1-methyl-3-diphenyl-5-phenylpyrrholone:—



On reduction with sodium and boiling amyl alcohol, these pyrrholones yield the corresponding dihydro-compounds or *pyrrholidones*—derivatives of tetrahydropyrrhole—



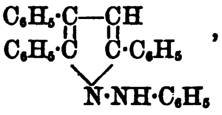
3-Diphenyl-5-phenyl-pyrrholidone (m. p. 201°).



1-Methyl-3-diphenyl-5-phenyl-pyrrholidone (m. p. 153·5°).

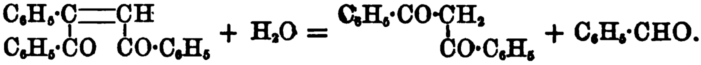
The pyrrholones also yield characteristic oxidation-products and bromine-derivatives, which have been analysed. The constitution of the oxidation-products has still to be determined.

By the action of phenylhydrazine on dibenzoylcinnamene, Japp and Huntly obtained (Trans., 1888, 184) a compound of the formula $C_{28}H_{22}N_2$. We regard this compound as most probably an anilidotriphenylpyrrhole of the constitution

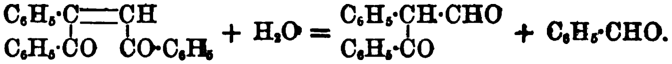


a view corresponding with that adopted by Knorr in the case of the compound prepared by him from phenylhydrazine and ethylic diacetosuccinate (*Annalen*, **236**, 295).

From the product of this reaction of dibenzoylcinnamene with phenylhydrazine, we succeeded in isolating two further compounds: a compound of the formula $C_{28}H_{22}N_2O$, apparently a monhydrazone of dibenzoylcinnamene; and a compound $C_{21}H_{16}N_2$, probably a triphenylpyrazole. The latter compound is formed from αβ-dibenzoylcinnamene with elimination of a benzoyl-group. According as the benzoyl-group is removed from the α- or from the β-carbon-atom, αβ-dibenzoylcinnamene will yield either dibenzoylmethane or phenylbenzoylacetaldehyde:—

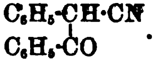
I. 

$$\begin{array}{l} C_6H_5\cdot C{=\!=}CH \\ C_6H_5\cdot CO\quad CO\cdot C_6H_5 \end{array} + H_2O = \begin{array}{l} C_6H_5\cdot CO\cdot CH_2 \\ \qquad\qquad CO\cdot C_6H_5 \end{array} + C_6H_5\cdot CHO.$$

II. 

$$\begin{array}{l} C_6H_5\cdot C{=\!=}CH \\ C_6H_5\cdot CO\quad CO\cdot C_6H_5 \end{array} + H_2O = \begin{array}{l} C_6H_5\cdot CH\cdot CHO \\ C_6H_5\cdot CO \end{array} + C_6H_5\cdot CHO.$$

Both these compounds would react with phenylhydrazine, eliminating 2 mols. of water, and yielding triphenylpyrazoles. The 1-3-5-triphenylpyrazole, from dibenzoylmethane and phenylhydrazine, has been prepared by Knorr and Laubmann (*Ber.*, **21**, 1206), and is quite distinct from our compound, which is, therefore, probably derived from phenylbenzoylacetaldehyde, and would consequently be either 1-3-4- or 1-4-5-triphenylpyrazole.

αβ-Dibenzoylcinnamene also reacts with hydroxylamine hydrochloride with elimination of a benzoyl-group. The resulting compound, $C_{15}H_{11}NO$ (m. p. 73—75°) is, as Dr. Claisen has kindly informed us, distinct from a diphenylisoxazol which he has prepared from dibenzoylmethane and hydroxylamine. It is, therefore, like the phenylhydrazine compound, probably derived from phenylbenzoylacetaldehyde, and would be either a diphenylisoxazol isomeric with Dr. Claisen's compound, or a nitrile of the formula  $\begin{array}{l} C_6H_5\cdot CH\cdot CN \\ C_6H_5\cdot CO \end{array}$.

These phenylhydrazine- and hydroxylamine-derivatives require further investigation.

PART II. EXPERIMENTAL.

Preparation of αβ-Dibenzoylcinnamene.

The method employed by Japp and Miller (*loc. cit.*) in preparing dibenzoylcinnamene, of gently warming a mixture of benzil and acetophenone with aqueous caustic potash, gives a very unsatisfactory yield. We find, however, that, by employing an alcoholic solution of potash, the yield may be raised to 80 per cent. of the theoretical amount. The following mode of conducting the reaction gave the best result:—

105 grams of benzil and 70 grams of acetophenone are introduced into a flask and dissolved, with the aid of heat, in a small quantity of alcohol, after which the flask is cooled with water, shaking it all the time to prevent the formation of large crystals of benzil. To the magma of benzil crystals thus obtained, a solution of 20 grams of caustic potash, dissolved in 300 grams of alcohol diluted with 30 grams of water, is added. The reaction begins at once, but it is necessary to warm the mixture gently on the water-bath in order to get all the benzil into solution. As soon as this point is reached, the flask is removed from the water-bath, and allowed to stand; in an hour or two the separation is complete. The crystalline substance is transferred to a funnel, washed with a little alcohol, with the aid of the filter-pump, until free from the dark-coloured mother liquor, and recrystallised once from boiling alcohol. It is then pure.*

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* We take this opportunity of recording an observation which we have made regarding the preparation of another of the condensation-compounds of diketones with ketones—acetonebenzil, $C_{17}H_{16}O_3$.

In the original description of the preparation of this compound by the action of a small quantity of caustic potash solution on a mixture of benzil and acetone (Japp and Miller, Trans., 1885, 21), it was stated that the use of an acetone purified by means of the bisulphite compound was indispensable in order to obtain any acetonebenzil at all.

Having occasion to prepare this substance, we purified some acetone by the above method and mixed the acetone, benzil, and aqueous caustic potash in the prescribed proportions, but were astonished to find that no action took place, even on long shaking; the benzil would not dissolve. A second quantity of potash was added, and then a third; but still there was no action. At last an incautious addition of potash caused a reaction to take place; but the process had gone too far, and *anhydr*acetonebenzil, $C_{17}H_{14}O_2$, was formed.

We then started a fresh experiment, using, as before, the prescribed proportions. Again no reaction occurred. We then added to the mixture two or three drops of alcohol. The benzil at once began to dissolve, as in the experiments of Japp and Miller, and after standing for two or three days, the solution had deposited large crystals of acetonebenzil.

Acetone can, therefore, be prepared so pure as not to react with benzil under the conditions described by Japp and Miller, and their statements as to the necessity of employing absolutely pure acetone require qualification.

A specimen of "acetone from the bisulphite-compound" purchased from Kahlbaum gave a good yield of acetonebenzil when treated with benzil and potash, *without any addition of alcohol.*

It is to be borne in mind that alcoholic potash in larger quantity converts acetonebenzil into anhydracetonedibenzil, $C_{31}H_{24}O_4$ (*ibid.*, p. 26).

[I venture to suggest the following explanation of these discrepant observations on the formation of acetonebenzil:—

The acetone-bisulphite compound which I prepared along with Dr. Miller in the course of our joint work was washed with commercial ether, in order to free it from the last traces of impurities from the crude acetone, and was then dried by exposure

The melting point was found at 129°, as given in the first paper.

A specimen, deposited by spontaneous evaporation from a mixture of chloroform and carbon bisulphide, was found by Mr. Tutton, who has had the kindness to examine crystallographically several of the compounds described in this paper, to consist of small, rhombic prisms. Mr. Tutton will publish his measurements separately (see next paper).

Molecular Weight of $\alpha\beta$-Dibenzoylcinnamene.—We determined the molecular weight of the substance by Raoult's method, using acetic acid as a solvent. The results are too high, but leave no doubt that the compound has the molecular weight corresponding with the formula, $C_{23}H_{26}O_2$:—

					Mol. wt.	
	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{22}H_{16}O_2$.
I.	0·623	31·118	2·002	0·22°	355	312
II.	0·217	21·535	1·008	0·11	357	,,
III.	0·6126	24·504	2·500	0·283	345	,,

The molecular depression of acetic acid was taken as 39.

Triphenylfurfuran and Triphenylchlorofurfuran.

As already mentioned, the compound $C_{22}H_{16}O$ (m. p. 92—93°), obtained by boiling $\alpha\beta$-dibenzoylcinnamene with hydriodic acid is to be regarded as triphenylfurfuran, and the compound $C_{22}H_{15}ClO$ (m. p. 115°), from $\alpha\beta$-dibenzoylcinnamene and alcoholic hydrochloric acid, as triphenylchlorofurfuran.

In accordance with this constitution, we find that these substances react neither with phenyldrazine nor with acetic anhydride.

Reduction of Triphenylchlorofurfuran with Sodium Amalgam.—An alcoholic solution of this compound was heated with sodium amalgam on the water-bath for four days, renewing the sodium amalgam from time to time. Analysis of the substance thus obtained showed that the reduction was not complete. The treatment with sodium amalgam was, therefore, continued for two days longer. The substance now crystallised in tufts of slender, colourless needles, indistinguishable from those of triphenylfurfuran, melting at 95—96°. This melting point is slightly higher than that previously observed for this compound. Analysis showed that it was pure triphenylfurfuran:

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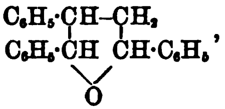
to the air before distilling it with sodium carbonate. It is conceivable that the crystals were incompletely dried, and that they retained a trace of alcohol from the commercial ether, which alcohol then passed over into the purified acetone, aiding the reaction in the manner above described.—F. R. J.]

	C.	H.	
Calculated for $C_{22}H_{16}O$	89·19	5·40	per cent.
Found	88·91	5·53	,,

Reduction of Triphenylfurfuran with Sodium and Amyl Alcohol.—Thirteen grams of triphenylfurfuran were dissolved in amyl alcohol, and the boiling solution was poured upon 11 grams of sodium. The liquid was kept boiling until all the sodium had disappeared, after which it was twice washed with water, separated, and distilled. After the amyl alcohol had been driven off, the distillation was continued under reduced pressure. A pale-yellow liquid passed over at 290—300° under a pressure of 75 mm.; the pressure was not quite constant owing to a slight evolution of gas. The compound is probably a tetrahydride,



but the analytical figures would also agree with those required by a hexahydride:

	Substance.	CO_2.	H_2O.
I............	0·2972	0·9536	0·1921
II............	0·2661	0·8536	0·1732

	Calculated for $C_{22}H_{20}O$.	Calculated for $C_{22}H_{22}O$.	Found. I.	Found. II.
C	88·00	87·42	87·50	87·48
H	6·67	7·28	7·18	7·23
O	5·33	5·30	—	—
	100·00	100·00		

Oxidation of Triphenylfurfuran with Nitric Acid.—Zinin oxidised lepiden to "acicular oxylepiden," by heating it with a mixture of acetic acid and nitric acid. We, therefore, subjected triphenylfurfuran to the same treatment, hoping to reconvert it into αβ-dibenzoylcinnamene, but obtained instead the mononitro-derivative of the latter compound.

One part of triphenylfurfuran was dissolved in 10 parts of boiling glacial acetic acid, and a mixture of 3 parts of concentrated nitric acid with 1 part of acetic acid was gradually added. The reaction was at first very violent, and red fumes were given off in great quantity. On pouring the product into water, the substance separated as an oil, which speedily solidified. It was purified by recrystallisation from alcohol, a process which could only be repeated three times (although a constant melting point had apparently not been reached), as a considerable part of the substance had been lost through an accident. It formed pale-yellow thin plates, softening about 140°, and melting at 145—147°. Analysis showed that it was a *mononitrodibenzoylcinnamene*, $C_{23}H_{15}O_2(NO_2)$ (*v. infra*).

Dibenzoylcinnamene treated in the same way with a mixture of nitric acid and acetic acid is quite unaltered; but when gently warmed with excess of concentrated nitric acid, it is converted into the foregoing mononitro-compound. The colour and crystalline form of the two preparations were identical; but the substance prepared from dibenzoylcinnamene melted somewhat higher than the other—namely at 155°, with previous softening at 150°—and was obviously purer.

	Substance.	CO_2.	H_2O.
I	0·2334	0·6314	0·0885
II	0·2053	0·5570	0·0848
III	0·2500	0·6753	0·0991

	Substance.		*v.*	*t.*	*p.*
IV	0·1408	dry N + NO	9·02 c.c.	26·5°	397 mm.
		„ N......	9·02 „	26·5	389 „
V	0·1710	dry N......	9·02 „	24·5	503 „
VI	0·1701	dry N + NO	9·02 „	23·0	491 „
		„ N......	9·02 „	23·5	466 „

	Calculated for $C_{22}H_{15}NO_4$.		Found.					
			I.	II.	III.	IV.	V.	VI.
C_{22} ..	264	73·95	73·77	73·99	73·66	—	—	—
H_{15}..	15	3·92	4·21	4·58	4·40	—	—	—
N ...	14	4·20	—	—	—	3·79	4·02	3·86
O_4...	64	17·93	—	—	—	—	—	—
	357	100·00						

Analyses I, II, IV, and V were made with the preparation from triphenylfurfuran; III and VI with that from dibenzoylcinnamene.

The reaction of triphenylfurfuran with nitric acid, therefore, resembles that of lepiden, in so far as the furfuran-derivative is oxidised to an unsaturated γ-diketone, but differs from it inasmuch as the resulting compound undergoes nitration in the process.

Molecular Weight of Triphenylfurfuran.—We determined the molecular weight of this compound by Raoult's method, using benzene as a solvent:—

				Mol. wt.	
Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{22}H_{16}O$.
I. 0·2913	16·205	1·797	0·335°	263	296
II. 0·5114	12·678	4·033	0·753	263	„

(Molecular depression of benzene = 49.)

Action of Heat on αβ-Dibenzoylcinnamene.

Dibenzoylcinnamene yields different compounds according to the temperature to which it is heated. One of these may be readily prepared by the following process.

150 grams of dibenzoylcinnamene were heated, in portions of 50 grams at a time, at a temperature of 310° (in diphenylamine vapour). The substance was contained in a thin-walled boiling-tube, which was surrounded by another larger boiling-tube in which was the diphenylamine, care being taken that the level of the hot vapour outside was well above that of the substance inside. The heating was continued for half-an-hour. During the process, gas was evolved from the melted substance; this is due to a secondary reaction which will be considered later on. The contents of the tube were poured while still liquid into a flask, and the united product from three such tubes was treated first with ether, which dissolved a dark colouring matter, but along with it some of the new substance; then it was extracted with a small quantity of boiling alcohol, after which the remainder was dissolved in boiling alcohol. The substance deposited from this last solution was practically pure, but was recrystallised from alcohol for analysis; the substance from the first two extracts—together about a sixth of the whole—was impure and had to be recrystallised. The total yield of pure substance was 70 per cent. of the weight of the dibenzoylcinnamene.

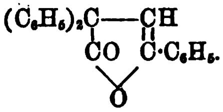
The new compound crystallises from alcohol in long, lustrous needles, or monoclinic prisms, starting from one point, melting without decomposition at 117—118°. Analysis showed that it was isomeric with dibenzoylcinnamene.

	Substance.	CO_2.	H_2O.
I	0·2108	0·6525	0·1011
II	0·1998	0·6177	0·0952

	Calculated for $C_{22}H_{16}O_2$.		Found.	
			I.	II.
C_{22}	264	84·62	84·41	84·31
H_{16}	16	5·13	5·32	5·29
O_2	32	10·25	—	—
	312	100·00		

The analyses were made with two different preparations.

The compound is, as we shall presently show, *triphenylcrotolactone*,



$$\begin{array}{l} (C_6H_5)_2C\text{---}CH \\ \qquad\quad\; CO \quad C\cdot C_6H_5. \\ \qquad\qquad O \end{array}$$

Phenylhydrazine in alcoholic solution does not react with it, either at 100° or at 150°. Acetic anhydride is without action even at 160°.

On one occasion in purifying triphenylcrotolactone, we isolated a small quantity of a sparingly soluble substance crystallising in minute, white needles. By means of the melting point (197—198°) and the characteristic colour reaction with concentrated sulphuric acid, we identified this substance with iso-$\alpha\beta$-dibenzoylcinnamene. This compound is more readily obtained in the reactions of $\alpha\beta$-dibenzoylcinnamene with some of the primary alkylamines (*v. infra*). Attempts to prepare it in larger quantity by heating $\alpha\beta$-dibenzoylcinnamene alone at various temperatures failed.

Molecular Weight of Triphenylcrotolactone.—The molecular weight was determined by Raoult's method in acetic acid solution:—

				Mol. wt.	
Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{22}H_{16}O_2$.
I. 0·328	15·211	2·156	0·25°	336	312
II. 0·384	15·020	2·557	0·31	322	,,

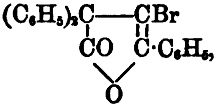
(Molecular depression of acetic acid = 39.)

Action of Bromine on Triphenylcrotolactone.—The substance was dissolved in chloroform and treated with two atomic proportions of bromine in the hope of obtaining an additive compound; but the addition of the bromine at once produced a strong evolution of hydric bromide. After getting rid of the chloroform in a vacuum-desiccator over solid paraffin and soda-lime, there remained an oil which solidified on exposure to air. As the compound had evidently been formed by substitution, it was recrystallised from boiling alcohol, from which it was deposited in broad, colourless needles melting constantly at 109°. A bromine determination (Carius) gave a result agreeing with the formula $C_{22}H_{15}BrO_2$:—

0·3957 gram substance gave 0·1887 gram AgBr.

	Calculated for $C_{22}H_{15}BrO_2$.	Found.
Br in 100 parts........	20·46	20·2

The compound probably has the constitution



but was not further studied.

Oxidation of Triphenylcrotolactone.—10 grams of the substance were dissolved in glacial acetic acid and oxidised with 20 grams of chromic anhydride, finishing the reaction on the water-bath. Water was then added and the oxidation-product, which was thus partly precipitated, was extracted with ether. The ethereal solution was shaken with sodium carbonate, which removed acetic and benzoic acids. After boiling off the ether on the water-bath, the residual yellow oil was distilled; it passed over between 295° and 300° (b. p. of benzophenone 296—297°), and on adding a minute fragment of a benzophenone crystal solidified almost completely. A small quantity of adhering oil was removed by absorption on a porous tile, after which the substance was redistilled under reduced pressure. It now solidified completely on touching it with a crystal of benzophenone. Thus purified, it showed the melting point of benzophenone (48°) and gave on analysis C, 85·36, H, 5·69 per cent. (Calculated for $C_{13}H_{10}O$, C, 85·72, H, 5·60 per cent.).

Reduction of Triphenylcrotolactone.—The substance was boiled for some minutes with fuming hydriodic acid in an open flask, then treated with water to remove hydriodic acid, boiled with dilute hydrogen sodium sulphite to get rid of iodine, again washed with water, and finally recrystallised from boiling alcohol, from which it was deposited in small, colourless needles melting constantly at 153°. Analysis gave figures agreeing with the formula of a dihydro-compound, $C_{22}H_{18}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·2162	0·6633	0·1143
II	0·2341	0·7179	0·1236

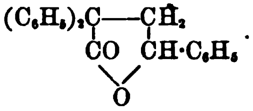
	Calculated for $C_{22}H_{18}O_2$.		Found.	
			I.	II.
C_{22}	264	84·08	83·67	83·63
H_{18}	18	5·73	5·87	5·86
O_2	32	10·19	—	—
	314	100·00		

The molecular weight was determined by Raoult's method, using benzene as a solvent:—

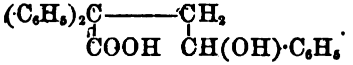
Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$.	Depression.	Mol. wt. Found.	Mol. wt. Calc. for $C_{22}H_{18}O_2$.
0·7331	21·476	3·413	0·548°	305	314

(Molecular depression of benzene = 49.)

The compound is to be regarded as *triphenylbutyrolactone*,



It is insoluble in aqueous potash, but dissolves in alcoholic potash, and after evaporating off the alcohol, a salt remains which is soluble in water. The solution of this salt gives with mineral acids a white precipitate which doubtless consists of *triphenyl-γ-hydroxybutyric acid*,



$$\begin{array}{ll}(C_6H_5)_2C\text{———} & CH_2 \\ \quad COOH & CH(OH)\cdot C_6H_5\end{array}.$$

When freshly precipitated, the acid readily dissolves in alkaline carbonates, but on drying, or even on standing under the solution, it loses this property and is found to have been re-converted into the lactone. Triphenylbutyrolactone is not altered by heating it with alcoholic ammonia to 150°, or by fusing it with ammonium acetate.

Triphenylcrotolactone was also reduced by heating it with hydriodic acid and amorphous phosphorus at 150°. The product was an oil which was not homogeneous. After distilling it under reduced pressure, a few crystals separated from the oily distillate; these were recrystallised from alcohol and were then found to melt at 146—147°; but the quantity was too small for examination, and the investigation of this product was therefore abandoned.

We also reduced triphenylcrotolactone by acting on its solution in boiling alcohol with metallic sodium. The solution thus obtained gave no precipitate on dilution with water; it contained the sodium salt of triphenyl-γ-hydroxybutyric acid. This acid, when liberated from the salt by the addition of a mineral acid, behaved as already described and was identified in the form of its lactone.

Action of Potash on Triphenylcrotolactone.—The substance was heated with alcoholic potash on the water-bath until a sample of the liquid, on evaporating off the alcohol and adding water, gave no turbidity. The alcohol was then expelled from the remainder, and the product was dissolved in water. Hydrochloric acid precipitated from the alkaline solution a colourless acid, which was purified by recrystallisation from a small bulk of methyl alcohol, from which it is deposited in transparent, colourless, rectangular plates. It melts at 182—183° without decomposition; between 220° and 230° it gives off gas (aqueous vapour), and at about 260° this evolution is rapid. Analysis of the acid dried at 100° showed that it had been formed from triphenylcrotolactone by the addition of a molecule of water:—

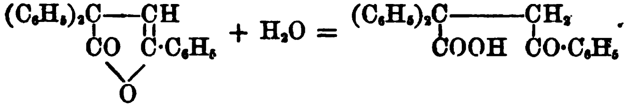
	Substance.	CO_2.	H_2O.
I........	0·2712	0·7896	0·1354
II........	0·1919	0·5607	0·0975

	Calculated for $C_{22}H_{18}O_3$.		Found.	
			I.	II.
C_{22}......	264	80·00	79·40	79·68
H_{18}......	18	5·45	5·54	5·64
O_3	48	14·55	—	—
	330	100·00		

The silver salt, prepared by precipitating the ammonium salt with silver nitrate, and dried over sulphuric acid, was of a greyish-white colour, and did not appear to be pure. It gave on analysis too low a result for carbon, and too high a result for silver. The value for the metal, however, shows beyond all doubt that the acid is monobasic:—

	Calculated for $C_{22}H_{17}O_3Ag$.	Found.
Ag in 100 parts.........	24·72	25·28

The acid is *α-diphenyl-β-benzoylpropionic acid*, formed according to the equation—



$$\begin{array}{ccc} (C_6H_5)_2C\text{---}CH & & (C_6H_5)_2C\text{------}CH_2 \\ \mid \qquad \| & + H_2O = & \mid \qquad \mid \\ CO \quad C\cdot C_6H_5 & & COOH \quad CO\cdot C_6H_5 \\ \diagdown \diagup & & \\ O & & \end{array}$$

Reduction of Diphenylbenzoylpropionic Acid.—A small quantity of the acid was boiled with fuming hydriodic acid, and the product freed from iodine by boiling with hydrogen sodium sulphate. It crystallised from alcohol in small, colourless needles melting at 154°, and was identical with the triphenylbutyrolactone already described.

A solution of the acid in aqueous caustic soda was treated on the water-bath for two days with a large excess of sodium amalgam. Hydrochloric acid precipitated from the solution triphenyl-γ-hydroxybutyric acid, which on drying and recrystallising from alcohol, was converted into triphenylbutyrolactone (*v. supra*).

Action of Phenylhydrazine on Diphenylbenzoylpropionic Acid.—The acid was heated with 2 molecular proportions of phenylhydrazine in alcoholic solution for a short time at 100°. On cooling, a quantity of unchanged substance was deposited, along with a red oil. The mixture was therefore heated for an hour at 150°. This time the liquid in the tube was filled with colourless needles melting at 185°. This substance was recrystallised from boiling alcohol, in which it is only sparingly soluble; it was deposited in well-shaped crystals, melting as before at 185°. Analysis showed that it had the formula $C_{28}H_{22}N_2O$:—

	Substance.	CO_2.	H_2O.
I........	0·1910	0·5840	0·0960
II........	0·2161	0·6607	0·1071

	Substance.		*v.*	*t.*	*p.*
III.....	0·1526	dry N + NO	13·5 c.c.	23·5°	530 mm.
		„ N......	13·5 „	23·5	513 „

	Calculated for $C_{28}H_{22}N_2O$.		Found.		
			I.	II.	III.
C_{28}......	336	83·58	83·38	83·38	—
H_{22}......	22	5·47	5·58	5·50	—
N_2.......	28	6·97	—	—	7·01
O........	16	3·98	—	—	—
	402	100·00			

The compound is formed according to the equation—

$$C_{22}H_{18}O_3 + C_6H_5{\cdot}NH{\cdot}NH_2 = C_{28}H_{22}N_2O + 2H_2O.$$

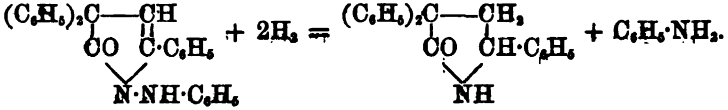
5 grams of this compound were reduced with 5 grams of sodium in boiling amyl alcohol. The solution was shaken with water, and the greater part of the amyl alcohol was distilled off under reduced pressure on the water-bath. From the concentrated solution a substance separated which, after recrystallisation from boiling alcohol, in which it is only sparingly soluble, formed colourless, slender needles melting at 201°. Analysis showed that it had the formula $C_{22}H_{19}NO$:—

	Substance.	CO_2.	H_2O.
I........	0·1862	0·5739	0·1022
II........	0·1907	0·5880	0·1067

	Substance.		*v.*	*t.*	*p.*
III.....	0·0969	dry N......	9·02 c.c.	19°	315 mm.
IV.....	0·1217	„ N + NO	9·02 „	19	402 „
		„ N......	9·02 „	19	383 „

	Calculated for $C_{22}H_{19}NO$.		Found.			
			I.	II.	III.	IV.
C_{22}	264	84·35	84·05	84·09	—	—
H_{19}	19	6·07	6·09	6·21	—	—
N	14	4·47	—	—	4·53	4·49
O	16	5·11	—	—	—	—
	3 3	100·00				

This compound is identical with 3-*diphenyl*-5-*phenylpyrrholidone* (*v. infra*), and its formation is best accounted for on the assumption that the phenylhydrazine-derivative of diphenylbenzoylpropionic acid is 1-*anilido*-3-*diphenyl*-5-*phenylpyrrholone* :—



The aniline was not looked for, as the amyl alcoholic mother liquor and distillate, which would have contained it, were unfortunately thrown away before the nature of the reaction was ascertained.

Action of Hydroxylamine on Diphenylbenzoylpropionic Acid.—5 grams of the acid were dissolved in alcohol with 3 grams of hydroxylamine hydrochloride, and heated in a sealed tube at 100° for half an hour. Addition of water precipitated a bulky substance, which dissolved readily in boiling alcohol, and separated in small, transparent crystals; these, after a further recrystallisation from the same solvent, melted constantly, with a slight evolution of gas, at 150—152°. We afterwards found that it could be more readily purified by recrystallisation from light petroleum. Analysis led to the formula $C_{22}H_{17}NO_2$:—

	Substance.	CO_2.	H_2O.
I........	0·2474	0·7294	0·1160
II........	0·2398	0·7084	0·1134

	Substance.		v.	t.	p.
III	0·1601	dry N + NO	9·02 c.c.	20°	472 mm.
		„ N......	9·02 „	20	457 „

	Calculated for $C_{22}H_{17}NO_2$.		Found.		
			I.	II.	III.
C_{22}	264	80·73	80·40	80·56	—
H_{17}	17	5·20	5·20	5·25	—
N........	14	4·28	—	—	4·03*
O_2	32	9·79	—	—	—
	327	100·00			

The compound is formed according to the equation

$$C_{22}H_{18}O_3 + NH_2{\cdot}OH = C_{22}H_{17}NO_2 + 2H_2O.$$

An attempt was then made to obtain a better yield of this compound by heating diphenylbenzoylpropionic acid with a large excess of hydroxylamine hydrochloride in dilute alcohol at 180° for two hours. There was a strong pressure in the tube on opening it. The alcohol was expelled on the water-bath, and water was added; the oily product was digested with sodium carbonate, washed, dissolved in hot alcohol, from which it separated in a crystalline form, and several times recrystallised from the same solvent. It formed long, flat, colourless needles melting at 142—143°. It is quite unacted upon by alcoholic potash. It has the formula $C_{22}H_{17}NO$, and has, therefore, been formed from the foregoing compound by the abstraction of an atom of oxygen. It is isomeric with triphenylpyrrholone (*v. infra*). The yield is not good.

	Substance.	CO_2.	H_2O.
I........	0·1955	0·6052	0·1023
II........	0·2801	0·8661	0·1452

	Substance.		*v.*	*t.*	*p.*
III	0·1008	dry N + NO	9·02 c.c.	15·5°	392 mm.
		,, N......	9·02 ,,	16	346 ,,
IV	0·1042	,, N......	9·02 ,,	17·5	374 ,,

	Calculated for $C_{22}H_{27}NO$.			Found.		
			I.	II.	III.	IV.
C_{22}	264	84·89	84·42	84·33	—	—
H_{17}	17	5·47	5·81	5·75	—	—
N	14	4·50	—	—	5·15	5·02
O	16	5·14	—	—	—	—
	311	100·00				

We are unable to account for the excess of nitrogen found in both determinations.

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* Determined by Dr. J. B. Tingle.

These two compounds are to be further studied.

Action of Heat on Diphenylbenzoylpropionic Acid.—A small quantity of the acid was heated at 310° (in diphenylamine vapour) until gas had almost ceased to be evolved from the melted substance, a process which required about ten minutes. Drops of water collected in the upper part of the test-tube containing the substance. The product was warmed with sodium carbonate solution and then recrystallised from alcohol, from which it was deposited in the characteristic needles of triphenylcrotolactone, melting at 117°. It is formed from the acid with the loss of a molecule of water, the process resembling, as already pointed out, the formation of the anhydrides of lævulic acid.

Action of Acetic Anhydride on Diphenylbenzoylpropionic Acid.—When the acid is heated with acetic anhydride at 150°, it parts with water, yielding triphenylcrotolactone, as in the foregoing reaction.

Distillation of αβ-Dibenzoylcinnamene and "Acicular Oxylepiden."

The evolution of gas described as occurring when dibenzoylcinnamene is heated in the preparation of triphenylcrotolactone is due to the decomposition of a portion of the latter substance. In order to study this reaction, and to obtain the compound formed, it is not necessary to prepare and isolate triphenylcrotolactone; it is sufficient to distil dibenzoylcinnamene: the transformation of this compound into the lactone and the decomposition of the latter take place in one operation, whilst the new compound passes over, and may be collected.

20 grams of dibenzoylcinnamene were distilled under reduced pressure, using an Anschütz flask,* and heating with a free flame. At first, gas was given off in such quantity that the pump was unable to keep pace with it, so that the manometer fell, and the operation had to be interrupted from time to time in order that the vacuum might be re-established. Later on, this evolution of gas slackened, and a yellow liquid passed over, solidifying in the receiver. The product was dissolved in ether. The solution, on standing, deposited large, transparent, yellow crystals, together with a brown oil; the latter could be removed by washing with ether. The crystals were heated with alcoholic potash, which removes any triphenylcrotolactone which they may contain; the substance was then reprecipitated with water and recrystallised, twice from alcohol and once from ether. It forms large, yellow, monoclinic prisms with the

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* In this flask the receiver is fused on to the tubulure. This arrangement is especially advantageous in distilling substances of high melting point, as, in the event of a stoppage, the tubulure can be heated throughout.

basal plane frequently so dominant as to render the crystals tabular. It melts at 92—93°, and dissolves in concentrated sulphuric acid with a bright yellow colour.

Analysis agreed with the formula $C_{21}H_{16}O$:—

	Substance.	CO_2.	H_2O.
I........	0·2126	0·6898	0·1082
II........	0·2374	0·7703	0·1198

	Calculated for $C_{21}H_{16}O$.		Found.	
			I.	II.
C_{21}......	252	88·74	88·48	88·49
H_{16}......	16	5·63	5·65	5·60
O.......	16	5·63	—	—
	284	100·00		

It is formed from dibenzoylcinnamene, or rather from the isomeric triphenylcrotolactone, by the elimination of carbon monoxide :—

$$C_{22}H_{16}O_2 + C_{21}H_{16}O + CO.$$

The mother liquor obtained in the treatment of the crude distillate with ether was evaporated to dryness, and the residue heated with alcoholic potash. From the potash solution, hydrochloric acid precipitated an acid which, after purification by redissolving in sodium carbonate, reprecipitating, and recrystallising from alcohol, melted at 182—183°, gave off water at 220—230°, and was identical with diphenylbenzoylpropionic acid. As a further proof, it was heated in phenanthrene vapour, and the product was dissolved in alcohol. The solution deposited pure triphenylcrotolactone melting at 117°.

It was evident, therefore, that a portion of the triphenylcrotolactone into which the dibenzoylcinnamene was converted had distilled over undecomposed, and had yielded with the potash diphenylbenzoylpropionic acid.

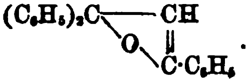
In order to ascertain whether the gas evolved in the reaction was, as required by the foregoing equation, carbon monoxide, a fresh quantity of dibenzoylcinnamene was heated, and the gas collected. The exact procedure employed will be described later in the case of the corresponding experiment with "acicular oxylepiden."

The volume of gas obtained was only about three-fourths of that required by the equation, but probably the decomposition was not complete, as the experiment with oxylepiden gave an almost theoretical result. A portion of the gas was analysed in a Frankland and Ward's apparatus. It gave no contraction with pyrogallate, showing that no air was mixed with the gas. Fuming sulphuric acid absorbed 3 per cent., and the remainder, as the following figures show, consisted of practically pure carbon monoxide :—

	Vol. at 0° and 760 mm.
Gas taken (after treatment with $H_2S_2O_7$) ..	8·73 c.c.
After adding O.........................	19·47 „
After explosion.........................	14·92 „
After absorption with KOH..............	6·24 „

	O.	Contraction.	CO_2.
Required for 1 vol. CO......	0·5	0·5	1
Found.....................	0·52	0·52	0·99

A constitution which might be ascribed to a compound formed from triphenylcrotolactone by the elimination of carbon monoxide is



This formula is in keeping with the fact that the compound is unacted on either by phenylhydrazine or by acetic anhydride. On the other hand, we find that a chloroform solution of the substance does not decolorise bromine, as an unsaturated compound like the foregoing might be expected to do. An attempt to oxidise it with chromic anhydride in acetic acid solution, so as to obtain a compound corresponding with Zinin's "oxyisolepiden," gave no result.

Reduction of the Compound $C_{21}H_{16}O$.—Four grams of the compound were reduced, in boiling alcoholic solution, with 8 grams of sodium. Water precipitated a thick, colourless oil, which could not be obtained in a crystalline form either by treatment with solvents or on long standing. It was therefore distilled under reduced pressure. It boiled at about 270° under 30 mm. pressure; the boiling point was not very constant. The product, a thick, colourless oil, solidified on standing. By recrystallisation from light petroleum it was obtained in small, colourless needles melting not very sharply at 86—92°. Analysis showed that it was a hydrocarbon; the figures would agree with the formula $C_{21}H_{18}$:—

Substance.	CO_2.	H_2O.
0·2036	0·6927	0·1235

	Calculated for $C_{21}H_{18}$.		Found.
C_{21}	252	93·33	92·78
H_{18}	18	6·67	6·74
	270	100·00	99·52

Such a hydrocarbon might either be a triphenylpropylene or a triphenyltrimethylene. The formation of the former of these might be accounted for on the supposition that in the reduction a triphenylpropyl alcohol is first formed, which in the subsequent distillation breaks off water, yielding triphenylpropylene. In the latter case it might be necessary to assume the existence of the trimethylene ring in the compound $C_{21}H_{16}O$.

An attempt was made to prepare a further quantity of the hydrocarbon, but this time the substance did not solidify, even after repeated distillation in a vacuum or on adding a crystal of the solid compound, so the investigation of the reaction was abandoned.

Distillation of "Acicular Oxylepiden."—The results obtained in the distillation of dibenzoylcinnamene do not, as was pointed out in the introductory part of this paper, preserve the analogy with Zinin's work. Following this analogy, we ought to have obtained, instead of the compound $C_{21}H_{16}O$, an isomeride of triphenylfurfuran, and instead of diphenylbenzoylpropionic acid, an isomeride of this acid. We therefore determined to repeat Zinin's work on the distillation of "acicular oxylepiden," in order to prepare and examine his "isolepiden" and "isoxylepidenic acid."

Lepiden was first prepared by Zinin's method, by heating benzoïn with fuming hydrochloric acid (saturated at 8°) at 130° during eight hours. The yield was only one-tenth of the weight of benzoïn employed; but we found that, by heating to 140° during the same period, this yield could be doubled. The lepiden was oxidised to "acicular oxylepiden" by treatment with nitric acid in acetic acid solution. We could not, by any process of recrystallisation, succeed in raising the melting point of this oxylepiden above 210—211°, whereas Zinin gives 220° as the melting point.

The following colour reactions of lepiden and "acicular oxylepiden" are not described by Zinin. Lepiden dissolves in concentrated sulphuric acid with a green colour; oxylepiden with a yellow colour, which almost instantly changes to a beautiful green.

13·4 grams of this oxylepiden were distilled from a weighed Anschütz flask under reduced pressure, heating with a free flame. There was, just as in the distillation of the dibenzoylcinnamene, a copious evolution of gas, which ceased towards the end of the operation. The distillate, poured out of the receiver, weighed 10 grams. The residue, partly remaining in the distilling flask, partly adhering to the attached receiver, weighed 2·4 grams. The loss was, therefore, 1 gram, whereas, according to the equation $C_{28}H_{20}O_2 = C_{27}H_{20}O + CO$, the loss from evolution of carbon monoxide should have been, for the foregoing quantity of oxylepiden, 0·96 gram—a sufficiently close approximation for an experiment of this character.

The distillate, which when cold formed a yellow, viscous mass, was treated with boiling ether, which caused it to become crystalline. The concentrated ethereal solution was poured off from the crystals, which were recrystallised, first from boiling alcohol, then, following Zinin's directions, from alcoholic potash, and then again from alcohol. This portion was employed for Analyses I and II. Part was recrystallised once more from ether and used for Analyses III and IV. The compound forms yellow crystals melting at 151° (150°, Zinin). We find that concentrated sulphuric acid dissolves it with a bright-red colour.

Analysis agreed with the formula $C_{27}H_{20}O$:—

	Substance.	CO_2.	H_2O.
I	0·2190	0·7202	0·1113
II	0·2600	0·8509	0·1313
III	0·2000	0·6597	0·0986
IV	0·1004	0·3306	0·0504

	Calculated for $C_{27}H_{20}O$.		Found.			
			I.	II.	III.	IV.
C_{27}	324	90·00	89·67	89·25	89·87	89·80
H_{20}	20	5·55	5·64	5·61	5·47	5·57
O......	16	4·45	—	—	—	—
	360	100·00				

Zinin's formula, $C_{28}H_{20}O$, requires C, 90·32, and H, 5·38 per cent., so that the analyses alone are hardly competent to decide between the two formulæ, although, so far as they go, they speak in favour of the formula adopted by us. Taken in conjunction, however, with the foregoing experiment on the loss of weight during distillation, and with another experiment, to be described presently, on the volume and nature of the gas evolved, they leave no doubt that the substance has the formula $C_{27}H_{20}O$, and that it is formed with elimination of a molecule of carbon monoxide, instead of being, as Zinin imagined, a product of deoxidation.

The ethereal extract from the distillate was treated, according to Zinin's directions, with alcoholic potash, in order to obtain the "isoxylepidenic acid." From the alkaline solution an acid was precipitated, which, after recrystallisation from alcohol, melted at 174°, and was indistinguishable from ordinary oxylepidenic acid prepared by the action of caustic potash on "tabular oxylepiden."* Zinin gives 166° as the melting point of his "isoxylepidenic acid."

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* The specimen of oxylepidenic acid with which we compared it, and which was measured by Mr. Tutton, melted at 176°. Zinin gives the melting point of this

Mr. Tutton had the kindness to make a crystallographical comparison of the acids from the two sources—*i.e.*, from the distillate and from "tabular oxylepiden"—and has fully established their identity (see following paper).

As an additional proof, we heated some of our "isoxylepidenic acid" in a test-tube in phenanthrene vapour. It behaved exactly like oxylepidenic acid, splitting off water and yielding "tabular oxylepiden," which, after recrystallisation from alcohol, showed the correct melting point of 136°.

We are therefore constrained to regard Zinin's supposed "isoxylepidenic acid" as nothing more than impure oxylepidenic acid. Under the influence of heat, the "acicular oxylepiden" is converted into "tabular oxylepiden," of which the greater part is decomposed, yielding "isolepiden," $C_{27}H_{20}O$, but a small quantity is carried over unchanged, and is converted into oxylepidenic acid in the subsequent treatment with caustic potash.

A small weighed quantity of "acicular oxylepiden" was then introduced into a tubulated distilling flask, the flask was exhausted with the Sprengel mercury pump, and then heated in a bath of powdered graphite. We were astonished to find, however, that under these circumstances no gas was evolved. A substance distilled and solidified in the upper part of the flask. After recrystallising this from alcohol, it melted at 210°, and gave with concentrated sulphuric acid the colour reaction of "acicular oxylepiden." This substance, therefore, provided local superheating is avoided, distils in the Sprengel vacuum unchanged, and is not even transformed into the tabular modification.

We therefore repeated the experiment, inserting through the india-rubber stopper of the distilling flask the neck of a bulb containing sodium bicarbonate. The tubulure of the flask was connected with the pump as before. After exhausting the air, the bicarbonate was gently heated, and as soon as the mercury in the fall-tube of the pump showed that atmospheric pressure had been re-established inside the flask, heat was applied to the graphite bath. This time gas was readily given off from the substance and was collected over caustic potash at the bottom of the fall-tube. When the evolution had ceased, the remainder of the gas in the apparatus was pumped out.

acid at 196°. Our specimens, both of this acid and of the "isoxylepidenic" acid, although beautifully crystallised, were coloured and evidently not quite pure. A further recrystallisation of the oxylepidenic acid from benzene raised the melting point to 180°; but here we were obliged to stop for want of substance; and for the same reason we were unable further to purify the "isoxylepidenic" acid. The melting point of the substance is greatly lowered by a very slight trace of impurity.

The same method was employed, as already mentioned, in the experiment with dibenzoylcinnamene. It has, of course, the disadvantage that if carbon dioxide were given off in the reaction it would be overlooked. We convinced ourselves, however, by a separate experiment in the case of dibenzoylcinnamene, that, with this substance at least, only the merest trace of carbon dioxide is formed.

In the present experiment, 0·2650 gram of dibenzoylcinnamene yielded 14·72 c.c. of gas at 0° and 760 mm. (The reaction $C_{28}H_{20}O_2 = C_7H_{20}O + CO$ requires 15·30 c.c.) Fuming sulphuric acid absorbed 2·4 per cent., and the remainder gave, on analysis, figures which showed that it consisted of nearly pure carbon monoxide :—

	Vol. at 0° and 760 mm.
Gas taken (after treatment with $H_2S_2O_7$)	7·35 c.c.
After adding O	26·48 ,,
After explosion	22·61 ,,
After absorption with KOH................	15·14 ,,

	O.	Contraction.	CO_2.
Required for 1 vol. CO	0·5	0·5	1·0
Found....................	0·54	0·53	1·02

Reduction of "Isolepiden."—The substance was reduced in boiling amyl-alcoholic solution with excess of sodium, and the product was distilled under a pressure of 30 mm., in the hope of obtaining a hydrocarbon $C_{27}H_{22}$, which would be the phenyl-derivative of the hydrocarbon $C_{21}H_{18}$ already described; but the only substance formed was Zinin's *tetrahydro-"isolepiden"* (m. p. 132°).

Action of Ammonia and Amines on αβ-Dibenzoylcinnamene and Triphenylcrotolactone.

Dibenzoylcinnamene is dissolved in hot alcohol and an excess of strong alcoholic ammonia is added to the hot solution. On standing, the liquid deposits well-shaped, colourless, rhombic crystals, tabular in habit, often forming thin plates. It melts at about 180°, but solidifies again almost immediately, and then does not melt again until the temperature has been raised to about 220°. This solidification corresponds with the conversion of the compound into an isomeride of higher melting point (*v. infra*).

The quantity of pure substance which had separated from the foregoing ammoniacal solution after standing over night was between 70 and 80 per cent. of the weight of dibenzoylcinnamene employed. An impure product was obtained from the mother liquor.

Analysis of the substance, dried at ordinary temperature, led to the formula $C_{28}H_{17}NO$.

	Substance.	CO_2.	H_2O.
I	0·2171	0·6780	0·1144
II	0·1979	0·6182	0·1058

Substance.		v.	t.	p.
III. 0·1101	dry N + NO	9·02 c.c.	19°	376 mm.
	„ N......	9·02 „	19	360 „
IV. 0·1754	dry N + NO	13·5 „	20	403 „
	„ N......	13·5 „	20·5	390 „

	Calculated for $C_{22}H_{17}NO$.		Found.			
			I.	II.	III.	IV.
C_{22}	264	84·89	85·17	85·19	—	—
H_{17}......	17	5·47	5·85	5·94	—	—
N.......	14	4·50	—	—	4·65	4·69
[illegible]......	16	5·14	—	—	—	—
	311	100·00				

The compound is formed from dibenzoylcinnamene according to the equation

$$C_{22}H_{16}O_2 + NH_3 = C_{22}H_{17}NO + H_2O.$$

We have not yet been able to ascertain its constitution, and propose provisionally to name it *dibenzoylcinnamenimide.*

The molecular weight was determined by Raoult's method, using as a solvent glacial acetic acid, in which the substance is soluble in the cold without decomposition, although on heating with this solvent it undergoes a change (see following paragraph):—

	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Mol. wt. Found.	Mol. wt. Calc. for $C_{22}H_{17}NO$.
I ..	0·322	13·888	2·318	0·27°	335	311
II ..	0·724	15·297	4·733	0·48	384	„
III ..	0·4484	21·230	2·112	0·253	326	„

(Molecular depression of acetic acid = 39.)

It is chiefly remarkable for the ease with which it is converted into an isomeric compound melting at 221°. This new compound is, as we shall show presently, a triphenylpyrrholone. The change takes place, as already mentioned, on heating the substance to its melting point; further, on boiling it with acetic acid, or acetic anhydride, or a mixture of equal volumes of sulphuric acid and water, or on heating it with an alcoholic solution of phenylhydrazine at 100°. Boiling with alcohol also effects the change, although the substance may be recrystallised from alcohol, provided that too protracted boiling is avoided.

From the foregoing it is evident that only those reactions which do not involve heating or rise of temperature can be trusted to throw light on the constitution of this compound, as otherwise the compounds obtained may be merely derivatives of triphenylpyrrholone. Thus, in reducing the compound in boiling alcoholic solution with metallic sodium, we obtained triphenylpyrrholidone, the dihydro-derivative of triphenylpyrrholone.

Action of Bromine on Dibenzoylcinnamenimide.—The compound was dissolved in chloroform, and a solution of bromine in the same menstruum was added. A yellow precipitate speedily separated, which was thoroughly washed with chloroform. It formed minute, yellow needles melting with strong decomposition at 199°. For analysis it was dried, first by brief exposure to the air, to get rid of the chloroform, and then over sulphuric acid. In the carbon and hydrogen determinations of this compound, as of the other bromine compounds mentioned in this paper, a silver spiral was employed to absorb the bromine.

Analysis agreed with the formula $C_{22}H_{17}NOBr_2$, showing that an additive compound had been formed:—

	Substance.	CO_2.	H_2O.
I.........	0·2386	0·4879	0·0870
II.........	0·2732	0·5573	0·0942

III. 0·2690 gram gave 0·2125 gram AgBr (Carius).

	Calculated for $C_{22}H_{17}NOBr_2$.		Found.		
			I.	II.	III.
C_{22}......	264	56·05	55·76	55·63	—
H_{17}.....	17	3·61	4·05	3·83	—
N......	14	2·97	—	—	—
O......	16	3·40	—	—	—
Br_2.....	160	33·97	—	—	33·61
	471	100·00			

Action of Alcoholic Potash on Dibenzoylcinnamenimide Dibromide.—Alcoholic potash readily dissolves the dibromide on boiling, the yellow colour of the compound disappearing before it goes into solution. On adding water, a substance was precipitated which, after recrystallisation from alcohol, melted at 221°, and had all the properties of triphenylpyrrholone. The identity was further confirmed by analysis: Calculated for $C_{22}H_{17}NO$, C, 84·89, H, 5·47; found, C, 84·76, H, 5·70.

The alcoholic potash had therefore removed bromine and converted the resulting dibenzoylcinnamenimide into triphenylpyrrholone.

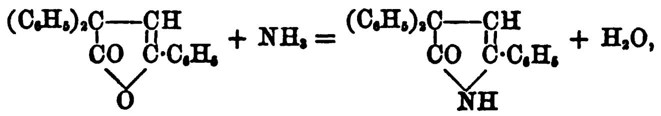
Action of Heat on Dibenzoylcinnamenimide: Formation of Triphenylpyrrholone.—A quantity of dibenzoylcinnamenimide was heated in a test-tube until it melted, re-solidified, and again melted at a higher temperature. In order to disintegrate it, it was poured, while still liquid, into a flask of alcohol, with which it was then boiled. The solution, which was filtered hot, deposited, on cooling, slender, white needles melting at 221°. The new compound is sparingly soluble even in boiling alcohol, more readily soluble in boiling amyl alcohol or glacial acetic acid. By spontaneous evaporation of its ethereal solution, it was obtained in slender, triclinic prisms. Analysis showed that it had the same composition as dibenzoylcinnamenimide.

	Substance.	CO_2.	H_2O.
I	0·2560	0·7966	0·1284
II	0·2946	0·9170	0·1435

Substance.		v.	t.	p.
III. 0·1240	dry N + NO	9·02 c.c.	22°	416 mm.
	„ N......	9·02 „	22	405 „
IV. 0·1097	dry N + NO	9·02 „	22	376 „
	„ N......	9·02 „	22·5	357 „

	Calculated for $C_{22}H_{17}NO$.		Found.			
			I.	II.	III.	IV.
C_{22}	264	84·89	84·86	84·89	—	—
H_{17}......	17	5·47	5·57	5·41	—	—
N.......	14	4·50	—	—	4·56	4·60
O	16	5·14	—	—	—	—
	311	100·00				

This compound is in reality derived from triphenylcrotolactone, as the following experiment shows:—Equal weights of dibenzoylcinnamene and triphenylcrotolactone were heated with the same volume of alcoholic ammonia in sealed tubes for 10 minutes at 100°, after which the tubes were quickly cooled. The dibenzoylcinnamene yielded only dibenzoylcinnamenimide; the triphenylcrotolactone was totally converted into the foregoing compound $C_{22}H_{17}NO$ melting at 221°, which is therefore formed according to the equation,



and would receive the name *triphenylpyrrholone*, or, more precisely, 3-*diphenyl*-5-*phenylpyrrholone*.

The identity of the triphenylpyrrholone thus obtained was confirmed by analysis: Calculated for $C_{22}H_{17}NO$, C, 84·89, H, 5·47, N, 4·50; found, C, 84·80, H, 5·57, N, 4·64 per cent.

The following experiment was made in order to ascertain whether the transformation of dibenzoylcinnamenimide into triphenylpyrrholone was attended by any change of weight:—2·830 grams of dibenzoylcinnamenide were heated at 240°, in a test-tube placed in a sulphuric acid bath, until the whole substance had melted to a clear liquid. Loss: 0·0120 gram (about 0·5 per cent.).

Triphenylpyrrholone does not react with acetic anhydride at 140°, or with phenylhydrazine in alcoholic solution at 100°. With bromine in chloroform solution it appears to form a very unstable additive compound which parts with its bromine on the evaporation of the solution at ordinary temperatures, leaving only the original substance in an impure state.

Molecular Weight of Triphenylpyrrholone.—The molecular weight was determined by Raoult's method, using acetic acid as a solvent:—

					Mol. wt.	
	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{22}H_{17}NO$.
I.	0·1932	27·173	0·711	0·087°	319	311
II.	0·3690	23·190	1·591	0·194	320	311

(Molecular depression of acetic acid = 39.)

These results leave no doubt that triphenylpyrrholone, like dibenzoylcinnamenimide, has the simple molecular weight.

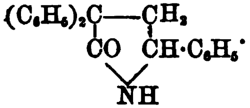
Reduction of Triphenylpyrrholone.—7·5 grams of the compound were dissolved in boiling amyl alcohol, and reduced with 4 grams of sodium. After shaking the amyl alcohol with water to remove the alkali, the reduction-product separated in crystals, and after recrystallisation from boiling alcohol, was obtained in a state of purity. It formed slender, colourless needles melting constantly at 201°. Analysis showed that it had the formula $C_{22}H_{19}NO$:—

	Substance.	CO_2.	H_2O.
I........	0·2272	0·7014	0·1252
II........	0·2001	0·6191	0·1097

	Substance.		*v*.	*t*.	*p*.
III....	0·1717	dry N + NO	13·5 c.c.	21·5°	389 mm.
		" N......	13·5 "	22	375 "

	Calculated for $C_{22}H_{19}NO$.		Found.		
			I.	II.	III.
C_{22}......	264	84·35	84·19	84·38	—
H_{19}......	19	6·07	6·12	6·09	—
N.......	14	4·47	—	—	4·59
O.......	16	5·11	—	—	—
	313	100·00			

The compound is therefore formed from triphenylpyrrholone by the addition of two atoms of hydrogen. It would thus be a *triphenylpyrrholidone—3-diphenyl-5-phenylpyrrholidone* :—



An attempt was made to prepare it by heating triphenylbutyrolactone with alcoholic ammonia; but, as already mentioned, no reaction took place even at a temperature of 150—160°.

The molecular weight was determined by Raoult's method, in acetic acid solution:—

				Mol. wt.	
Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{22}H_{19}NO$.
0·264	18·882	1·398	0·178°	306	313

(Molecular depression of acetic acid = 39.)

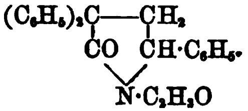
Triphenylpyrrholidone was heated with acetic anhydride for one hour at 150°; but, although some action had taken place, we did not succeed in obtaining a pure product. However, by heating the compound with acetic anhydride and fused potassium acetate (1 part of triphenylpyrrholidone, 1 part of fused acetate, and 4 parts of acetic anhydride) for two hours at 180°, an acetyl-derivative was prepared. There is considerable pressure in the tube on opening. The compound was precipitated with water and recrystallised from light petroleum, in which it is readily soluble. It was deposited in well-formed crystals, embedded in a little oily matter, from which they were separated by recrystallisation from the same solvent; they were then colourless, and melted at 105°. From a concentrated solution it separates in nodules.

Analysis showed that a monacetyl-derivative had been formed :—

	Substance.	CO_2.	H_2O.
I........	0·2192	0·6526	0·1186
II........	0·2090	0·6244	0·1149

	Calculated for $C_{24}H_{21}NO_2$.		Found.	
			I.	II.
C_{24}	288	81·13	81·19	81·47
H_{21}	21	5·92	6·01	6·10
N..........	14	3·94	—	—
O_2	32	9·01	—	—
	355	100·00		

The compound has the constitution



Action of Methylamine on αβ-Dibenzoylcinnamene.—Dibenzoylcinnamene was dissolved in alcohol, and an alcoholic solution of methylamine was added to the hot solution. The liquid, on cooling, deposited lustrous, colourless, triclinic prisms, melting at 143°, whilst a further small quantity was obtained on concentrating the mother liquor. Analysis showed that the compound had the formula $C_{23}H_{19}NO$:—

	Substance.	CO_2.	H_2O.
I........	0·2154	0·6680	0·1162
II........	0·2646	0·8223	0·1424

	Substance.		v.	t.	p.
III....	0·1661	dry N + NO	9·02 c.c.	16°	523 mm.
		„ N......	9·02 c.c.	17	513 „

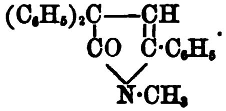
	Calculated for $C_{23}H_{19}NO$.		Found.		
			I.	II.	III.
C_{23}......	276	84·92	84·57	84·75	—
H_{19}......	19	5·85	5·99	5·97	—
N	14	4·31	—	—	4·38
O	16	4·92	—	—	—
	325	100·00			

The compound is formed according to the equation

$$C_{22}H_{16}O_2 + NH_2{\cdot}CH_3 = C_{23}H_{19}NO + H_2O.$$

The yield was 96 per cent. of the theory.

This compound is also formed by the abstraction of a molecule of water from the methylamide of diphenylbenzoylpropionic acid (*v. infra*). It is therefore 1-*methyl*-3-*diphenyl*-5-*phenylpyrrholone*,



$$\begin{array}{l}(C_6H_5)_2C\text{---}CH \\ \quad\quad\;\; CO \quad C\cdot C_6H_5 \\ \quad\quad\quad\;\; N\cdot CH_3\end{array}.$$

As this would make the compound an analogue of triphenylpyrrholone, which is formed from dibenzoylcinnamenimide under the influence of heat, we thought that it might have been formed by the transformation of a methyl analogue of dibenzoylcinnamenimide, and endeavoured to obtain this compound by conducting the reaction at a lower temperature. A very dilute solution of dibenzoylcinnamene was cooled to 40° (below this temperature the substance separated) and an excess of an alcoholic solution of methylamine was added. After standing for about a week, crystals began to be deposited; after another week, the quantity did not appear to increase. The crystals were examined crystallographically by Mr. Tutton, who found that they were of two kinds: (1) in small quantity, large crystals of the foregoing triclinic methyltriphenylpyrrholone; and (2), as chief product, colourless, tabular, rhombohedral-hexagonal crystals. Determinations of the melting points of the two kinds, made simultaneously with the same thermometer, showed that the rhombohedral-hexagonal form melted sharply at 138°, the triclinic form less sharply at 141—142°.

We, at first, thought that this rhombohedral-hexagonal form was the expected analogue of dibenzoylcinnamenimide, and that in the first reaction it had been changed at the temperature of the reaction into methyltriphenylpyrrholone; but the following experiment showed that this view was untenable.

Triclinic triphenylpyrrholone was distilled under a pressure of 30 mm. without showing the slightest decomposition.* The distillate was recrystallised from alcohol. The crystals melted at 138° and showed, according to Mr. Tutton, the optical properties of the rhombohedral-hexagonal substance. It was, therefore, highly improbable that a compound which had thus been formed from the triclinic substance at the high temperature of the distillation could have been converted into the same triclinic substance at the temperature of boiling alcohol.

Analysis showed that the rhombohedral-hexagonal compound had, like the triclinic compound, the formula $C_{23}H_{19}NO$. Calculated, C, 84·92, H, 5·85, N, 4·31; found, C, 84·60, H, 5·86, N, 4·15.

---

* The boiling point was not observed, as the end of the mercurial thread was concealed by the cork, and we did not think it necessary on this account to repeat the experiment, which was made with the totally different object of ascertaining whether the substance would be changed into another modification.

We regard these two substances as dimorphic modifications of the same compound. Thus, they both yield with bromine at ordinary temperatures the same monobromo-derivative (*v. infra*). Furthermore, in the case of the corresponding ethyltriphenylpyrrholone, we have obtained two similar modifications which we have succeeded in changing backwards and forwards, the one into the other, under circumstances which exclude the possibility of isomeric change in two opposite directions.

The molecular weight of the two crystalline modifications of methyltriphenylpyrrholone was determined by Raoult's method. Different solvents were employed:—

a. In Acetic Acid Solution.

					Mol. wt.	
	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{23}H_{19}NO$.
I..	0·357	20·0	1·785	0·21°	331	325
II..	0·4835	17·739	2·725	0·31	343	,,
III..	0·2695	16·787	1·605	0·20	313	,,

(Molecular depression of acetic acid = 39.)

b. In Benzene Solution.

IV..	0·2156	24·728	0·8719	0·147	291	,,
V..	0·3878	20·646	1·878	0·303	304	,,

(Molecular depression of benzene = 49.)

c. In Nitrobenzene Solution.

VI..	0·6330	25·415	2·490	0·593	307	,,

(Molecular depression of nitrobenzene = 73.)

Determination I was made with the triclinic, the remainder with the rhombohedral-hexagonal modification.

Methyltriphenylphyrrholone is unacted on by acetic anhydride at 160°, or by phenylhydrazine at 150°.

Action of Bromine on Methyltriphenylpyrrholone.—When a solution of bromine in chloroform was added to a chloroform solution of triclinic methyltriphenylpyrrholone, the colour of the bromine disappeared until nearly one molecular proportion of bromine had been added. The solution was allowed to evaporate to dryness in a vacuum-desiccator over soda-lime and solid paraffin. A hard, crystalline mass remained, which was dissolved in carbon bisulphide; it separated from the solution, on spontaneous evaporation, in large, lustrous, yellow, monoclinic prisms, some of which were as much as an inch long and one-third of an inch thick, melting constantly at 150°. Recrystallisation from alcohol removed the yellow colour, and the substance was deposited from this solvent in acicular prisms, very much striated, also melting at 153°. The yield is very good: 10 grams of methyltriphenylpyrrholone gave 11 grams of pure recrystallised substance.

Analysis showed that a monobromo-substitution compound, $C_{23}H_{18}BrNO$, had been formed:—

	Substance.	CO_2.	H_2O.
I........	0·2240	0·5599	0·0946
II........	0·2401	0·5974	0·0995

III. 0·2899 gram gave 0·1366 gram AgBr (Carius).
IV. 0·3961 „ 0·1857 „ „

	Calculated for $C_{23}H_{18}BrNO$.		Found.			
			I.	II.	III.	IV.
C_{23}....	276	68·32	68·17	67·85	—	—
H_{18}....	18	4·46	4·69	4·60	—	—
Br....	80	19·80	—	—	20·04	19·94
N.....	14	3·46	—	—	—	—
O.....	16	3·96	—	—	—	—
	404	100·00				

The same experiment was then made with rhombohedral-hexagonal methyltriphenylpyrrholone. The bromine-derivative obtained was absolutely identical in appearance and melting point with the foregoing. The identity was completely established by a crystallographical comparison of the crystals from the two sources by Mr. Tutton.

Methyltriphenylmonobromopyrrholone underwent no change when heated with alcoholic potash or alcoholic ammonia for one hour at 150—160°.

Reduction of Methyltriphenylpyrrholone.—3·2 grams of methyltriphenylpyrrholone were reduced in boiling amyl-alcoholic solution with 1·4 gram of metallic sodium. The resulting solution was diluted with ether, shaken with water, separated, and distilled until all the ether and a considerable quantity of the amyl alcohol had passed over. The new compound separated in slender colourless needles, which were recrystallised from alcohol. They now melted constantly at 153·5°.

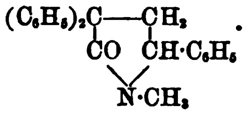
Analysis showed that a dihydro-derivative had been formed:—

	Substance.	CO_2.	H_2O.
I........	0·1982	0·6115	0·1180
II........	0·2288	0·7072	0·1384

	Substance.		v.	t.	p.
III....	0·1424	dry N + NO	9·02 c.c.	24·5°	454 mm.
		„ N......	9·02 „	24·5	419 „

	Calculated for $C_{23}H_{21}NO$.		Found.		
			I.	II.	III.
C_{23}......	276	84·41	84·14	84·29	—
H_{21}......	21	6·42	6·61	6·72	—
N	14	4·28	—	—	4·19
O	16	4·89	—	—	—
	327	100·00			

The compound is 1-*methyl*-3-*diphenyl*-5-*phenylpyrrholidone*,



The molecular weight was determined by Raoult's method, using acetic acid as a solvent:—

	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$	Depression.	Found.	Calc. for $C_{23}H_{21}NO$.
I..	0·366	21·02	1·741	0·205°	331	327
II..	0·725	25·247	2·871	0·33	339	„

(Molecular depression of acetic acid = 39.)

Oxidation of Methyltriphenylpyrrholone.—Ten grams of methyltriphenylpyrrholone were dissolved in warm acetic acid, and a saturated aqueous solution of 20 grams of chromium trioxide was gradually added. The temperature rose to the boiling point of the mixture, and a precipitate which was at first formed disappeared after all the chromium trioxide had been added. On adding water a yellowish oil was precipitated, which was extracted with ether. The ethereal solution was shaken with sodium carbonate solution, which removed some benzoic acid. After evaporating off the ether, an oil was left, which began to solidify. It was heated with acetic acid, but so as to leave a portion of the crystals undissolved; on standing, a crystalline substance was deposited. This was recrystallised from dilute alcohol, from which it separated in small, colourless, six-sided plates, melting without decomposition at 167°.

Analysis gave figures agreeing with the formula $C_{23}H_{19}NO_3$:—

	Substance.	CO_2.	H_2O.
I........	0·2386	0·6746	0·1171
II........	0·2517	0·7101	0·1233

	Substance.		v.	t.	p.
III....	0·1788	dry N + NO	9·02 c.c.	25·5°	552 mm.
		,, N......	9·02 ,,	25·5	491 ,,

	Calculated for $C_{23}H_{19}NO_3$.		Found.		
			I.	II.	III.
C_{23}......	276	77·31	77·10	76·94	—
H_{19}......	19	5·32	5·45	5·44	—
N	14	3·92	—	—	3·98*
O_3	48	13·45	—	—	—
	357	100·00			

This compound is to be further studied.

Action of Methylamine on Triphenylcrotolactone.—A strong alcoholic solution of methylamine dissolved triphenylcrotolactone with rise of temperature. In order to finish the reaction, the mixture was heated for half-an-hour at 100°, after which it was poured into water. Some difficulty was experienced in purifying the precipitated substance; but recrystallisation from ether was found to give the best results, and by this means it was ultimately obtained in small, colourless plates melting constantly at 156°.

Analysis gave numbers pointing to a compound $C_{23}H_{21}NO_3$, formed by the direct union of triphenylcrotolactone and methylamine. The percentage of carbon found is somewhat too high; but the behaviour of the compound on heating (*v. infra*) leaves no doubt as to its composition and nature:—

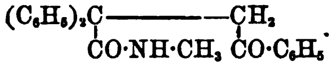
	Substance.	CO_2.	H_2O.
I........	0·2796	0·8278	0·1581
II........	0·2244	0·6673	0·1284

	Substance.		v.	t.	p.
III....	0·1635	dry N + NO	9·02 c.c.	20°	511 mm.
		,, N......	9·02 ,,	20	465 ,,

* Determined by Dr. Tingle.

	Calculated for $C_{23}H_{21}NO_2$.		Found.		
			I.	II.	III.
C_{23}......	276	80·47	80·74	81·10	—
H_{21}......	21	6·12	6·28	6·35	—
N.......	14	4·08	—	—	4.14*
O_2	32	9·33	—	—	—
	343	100·00			

The compound is the *methylamide of diphenylbenzoylpropionic acid*,



$$\begin{array}{ll}(C_6H_5)_2C & \!\!\!\!\text{———}\;CH_2 \\ \quad\; | & \quad\;\; | \\ CO{\cdot}NH{\cdot}CH_3 & CO{\cdot}C_6H_5.\end{array}$$

When it is heated in diphenylamine vapour it gives off gas (aqueous vapour), and is converted into methyltriphenylpyrrholone. The product, after recrystallising twice from alcohol, melted at 138°, and gave on analysis C, 84·34, H, 5·82. Calculated for $C_{23}H_{19}NO$: C, 84·92, H, 5·85 per cent. The modification was the triclinic, although the melting point is that of the rhombohedral-hexagonal variety ; possibly the lowering of the melting point by 5° was due to imperfect purification.

Action of Ethylamine on αβ-Dibenzoylcinnamene.—A hot saturated alcoholic solution of dibenzoylcinnamene was mixed with an alcoholic solution of ethylamine. On cooling, well-shaped triclinic prisms, isomorphous or morphotropic with triclinic methyltriphenylpyrrholone, were deposited. They had a faint yellowish tinge, which the purified compound does not display, and melted at 122—123°. Analysis, which was made without further recrystallising the substance, so as to avoid a possible change into another modification, gave figures agreeing with the expected formula $C_{24}H_{21}NO$:—

	Substance.	CO_2.	H_2O.
I........	0·2601	0·8032	0·1435

	Substance.		v.	t.	p.
II	0·1596	dry N + NO	9·02 c.c.	20°	508 mm.
		„ N......	9·02 „	20	457 „

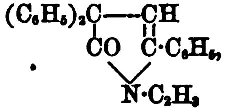
	Calculated for $C_{24}H_{21}NO$.		Found.	
			I.	II.
C_{24}........	288	84·96	84·21	—
H_{21}........	21	6·19	6·13	—
N.........	14	4·13	—	4·20
O.........	86	4·72	—	—
	339	100·00		

---

* Determined by Dr. Tingle.

Under a pressure of 38 mm., the substance boils at 312—314° without decomposition.

Another mode of formation from the ethylamide of diphenylbenzoylpropionic acid, to be described later, shows that the compound has the constitution



and is therefore an *ethyltriphenylpyrrholone.*

On repeating the experiment on the action of ethylamine on dibenzoylcinnamene, but employing a more dilute solution and a lower temperature, a compound of the same composition as the above, but crystallising in monoclinic prisms and melting at 129°, was obtained. We at first regarded this compound as an isomeride of the triclinic compound; but the following experiments show that the two substances are merely dimorphic modifications of the same compound:—

1. A quantity of the monoclinic compound was heated in diphenylamine vapour for 15 minutes. The solution in hot alcohol deposited *triclinic* crystals.

2. The triclinic compound was heated in diphenylamine vapour for half-an-hour. On recrystallising the product from alcohol, a mixture of *monoclinic* crystals with small crystals which appeared to be unchanged triclinic modification was obtained.

The heating has therefore, in all probability, nothing to do with the change, and the production of the one or the other modification depends on unascertained conditions of concentration and temperature prevailing during the recrystallisation.

Of the following determinations of the molecular weight by Raoult's method, employing acetic acid as a solvent, Nos. I and II were made with the triclinic, III and IV with the monoclinic variety:—

					Mol. wt.	
	Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$.	Depression.	Found.	Calc. for $C_{24}H_{21}NO$.
I..	0·3413	19·05	1·791	0·211°	331	339
II..	0·4650	22·748	2·044	0·243	328	,,
III..	0·4240	22·091	1·919	0·209	358	,,
IV..	0·5280	21·873	2·414	0·266	354	,,

(Molecular depression of acetic acid = 39.)

These figures leave no doubt that both varieties have the simple molecular formula.

Action of Bromine on Ethyltriphenylpyrrholone.—The triclinic variety was used for this reaction, and the operation was conducted exactly as in the case of the methyl-compound. The bromine-derivative was recrystallised from carbon bisulphide, from which solution it was deposited in yellow, monoclinic prisms, which became opaque on keeping. For analysis it was recrystallised from alcohol, from which it separated in colourless, thick needles melting at 142°, which was also the melting point of the yellow prisms. It has the formula $C_{24}H_{20}BrNO$:—

	Substance.	CO_2.	H_2O.
I	0·1920	0·4872	0·0866

II. 0·2792 gram gave 0·1252 AgBr (Carius).

	Calculated for $C_{24}H_{20}BrNO$.		Found.	
			I.	II.
C_{24}	288	68·90	69·20	—
H_{20}	20	4·78	5·01	—
Br	80	19·14	—	19·05
N	14	3·35	—	—
O	16	3·83	—	—
	418	100·00		

The compound is *ethyltriphenylmonobromopyrrholone.*

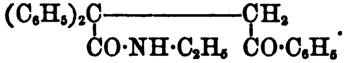
Action of Ethylamine on Triphenylcrotolactone.—The two substances were heated together in alcoholic solution in a sealed tube for half-an-hour at 100°. On adding water, an oil was precipitated, which was extracted with ether. By spontaneous evaporation, the ethereal solution deposited the new compound in silky needles; these, after further recrystallisation from ether, melted at 128—130°. At 240°, the compound gives off water.

Analysis showed that it had the formula $C_{24}H_{23}NO_2$, having been formed by the direct union of triphenylcrotolactone and ethylamine:—

	Substance.	CO_2.	H_2O.
I	0·2351	0·6937	0·1336
II	0·2074	0·6110	0·1191

	Calculated for $C_{24}H_{23}NO_2$.		Found.	
			I.	II.
C_{24}	288	80·67	80·47	80·34
H_{23}	23	6·44	6·31	6·38
N	14	3·97	—	—
O_2	32	8·92	—	—
	357	100·00		

The compound is the *ethylamide of diphenylbenzoylpropionic acid*,



$$\begin{array}{ll}(C_6H_5)_2C\text{———————} & CH_2 \\ \qquad\quad | & \;| \\ \qquad CO\cdot NH\cdot C_2H_5 & CO\cdot C_6H_5\end{array}.$$

On heating it in phenanthrene vapour (340°), it gave off water. The heating was continued for 15 minutes, and the product was twice recrystallised from alcohol. The solution deposited triclinic crystals of ethyltriphenylpyrrholone melting at 123°, which had thus been formed from the ethylamide with elimination of water.

Action of Propylamine on Dibenzoylcinnamene.—Propylamine does not react with dibenzoylcinnamene so readily as methylamine and ethylamine, so that it was found necessary to heat the two substances together in alcoholic solution at 100° in order that the reaction might take place. The *propyltriphenylpyrrholone*, $C_{25}H_{23}NO$, is deposited from its hot alcoholic solution in colourless, rhombic prisms melting at 104—105°. On one occasion, it was obtained by spontaneous evaporation in monoclinic prisms melting at 95—98°, isomorphous with the monoclinic form of ethyltriphenylpyrrholone; but we were unable to prepare this modification a second time.

Analysis of the rhombic crystals gave figures pointing to the formula $C_{25}H_{23}NO$:—

	Substance.	CO_2.	H_2O.
I	0·2355	0·7282	0·1360

Substance.		*v*.	*t*.	*p*.
II. 0·1528	dry N + NO	9·02 c.c.	23°	454 mm.
	„ N......	9·02 „	23·5	435 „

	Calculated for $C_{25}H_{23}NO$.		Found.	
			I.	II.
C_{25}	300	84·99	84·33	—
H_{23}........	23	6·51	6·41	—
N	14	3·97	—	3·99
O	16	4·53	—	—
	353	100·00		

On one occasion, when a saturated alcoholic solution of dibenzoylcinnamene was heated with excess of propylamine for half an hour at 100°, the liquid deposited, on standing, a substance crystallising in minute needles. The mother liquor, poured off from these needles, at once deposited crystals of rhombic propyltriphenylpyrrholone. The needles, after recrystallisation from boiling alcohol, in which they are only sparingly soluble, were again deposited in the same acicular form, and melted constantly at 197—198°. They give a very characteristic reaction with concentrated sulphuric acid, dissolving with a yellowish-green colour which changes to brown and finally to a beautiful red; this reaction is best seen with a small quantity of the substance.

This compound, which does not contain nitrogen, gave on analysis figures agreeing with the formula $C_{22}H_{16}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·1221	0·3795	0·0598
II	0·1004	0·3115	0·0463

	Calculated for $C_{22}H_{16}O_2$.		Found. I.	Found. II.
C_{22}	264	84·62	84·77	84·61
H_{16}	16	5·13	5·44	5·12
O_2	32	10·25	—	—
	312	100·00		

It is, therefore, isomeric with $\alpha\beta$-dibenzoylcinnamene. We have already mentioned that we regard it as probably the analogue of Zinin's "octahedral oxylepiden" and as the fumaroïd modification of dibenzoylcinnamene. We propose to name it *isodibenzoylcinnamene.*

It was also obtained, along with ethyltriphenylpyrrholone, by heating dibenzoylcinnamene with ethylamine in alcoholic solution, and in very small quantity in the preparation of triphenylcrotolactone by heating dibenzoylcinnamene alone (*v. supra*). In both cases, it was identified by its melting point, and by the characteristic colour test with sulphuric acid.

Action of Allylamine on Dibenzoylcinnamene.—Dibenzoylcinnamene readily reacts with allylamine when the two substances are heated together in alcoholic solution for a short time at 100° in a sealed tube, yielding *allyltriphenylpyrrholone*, $C_{25}H_{21}NO$, which crystallises from alcohol in monoclinic prisms melting at 110—112° and closely resembling in their crystallographical characters the monoclinic ethyl and propyl compounds.

	Substance.	CO_2.	H_2O.
I	0·2178	0·6802	0·1183
II	0·2517	0·7861	0·1321

		v.	*t.*	*p.*
III. 0·1759	dry N + NO	9·02 c.c.	18°	507 mm.
	„ N......	9·02 „	18	487 „

	Calculated for $C_{25}H_{21}NO$.		Found.		
			I.	II.	III.
C_{25}	300	85·47	85·17	85·17	—
H_{21}	21	5·98	6·03	6·05	—
N	14	3·99	—	—	3·95
O	16	4·56	—	—	—
	351	100·00			

Action of Phenylhydrazine on Dibenzoylcinnamene.

This reaction was first studied by Japp and Huntly (Trans., 1888, 184), who obtained a compound of the formula $C_{28}H_{23}N_2$,* which we regard as an anilidodtriphenylpyrrhole (*v. supra*). As the yield of this compound is small, and a large quantity of oily matter is formed at the same time, we resolved to study the reaction more thoroughly.

Dibenzoylcinnamene and phenylhydrazine, in the proportion of 1 mol. of the former to 2 mols. of the latter, were heated in alcoholic solution in sealed tubes for one hour at 100°. Gas escaped from the tubes on opening, and a quantity of the yellow insoluble anilidotriphenylpyrrhole had separated. The mother liquor was concentrated by boiling, and filtered from a further quantity of the yellow compound which had been formed during this process. The concentrated liquor deposited, on cooling, a yellow oil, which did not solidify even on long standing. The supernatant alcoholic solution (*a*) was therefore poured off from the oil (*b*).

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* Concerning this compound, Japp and Huntly (*loc. cit.*) state: "It melted, with blackening and decomposition, at 231—232°." A further examination has shown us that practically any melting point between 220° and 255° can be obtained, according as the temperature is raised slowly or rapidly.

[While on the subject of melting points, I take the opportunity of correcting the melting points of three compounds described in a paper, "Action of Nitriles on Benzil" (Japp and Tresidder, *Ber.*, 16, 2652; also Abstr., 1884, 313). These melting points are all given too low, and as the fresh determinations have been made with the original specimens of substance, I can only surmise that the mistake was due to an unnoticed defect in the thermometer employed. This thermometer has, in the meantime, unfortunately been broken.

The new melting points are:—

1. Compound $C_{30}H_{22}N_2O_3$ (from propionitrile and benzil); m. p. 207° (instead of 197°).
2. Compound $C_{28}H_{22}N_2O_3$ (from benzonitrile and benzil: sol. alcohol); m. p. 176° (instead of 168°).
3. Compound $C_{28}H_{21}NO_3$ (from benzonitrile and benzil; insol. alcohol); m. p. 237° (instead of 225°).

The regular increase in the amount of error with the rise in temperature suggests that the thermometer had a conical bore.—F. R. J.]

The oil (*b*) was treated with ether, which dissolved most of it, leaving a yellow crystalline substance. The ethereal extract left, on spontaneous evaporation, more of the crystalline substance embedded in oil; this latter was again removed with ether, and the ethereal solution of the oil allowed to stand, when it yielded a further quantity of the crystalline substance. The united crystalline substance was then recrystallised, first, several times from boiling alcohol, in which it is only sparingly soluble, afterwards from boiling glacial acetic acid, in which it dissolves more readily. It formed slender, yellow needles melting at 173—174°.

Analysis showed that it had the composition of a *monohydrazone of dibenzoylcinnamene*, $C_{22}H_{16}O(N_2H{\cdot}C_6H_5)$:—

	Substance.	CO_2.	H_2O.
I........	0·2140	0·6544	0·1117
II........	0·1932	0·5907	0·0983

	Substance.		*v.*	*t.*	*p.*
III....	0·1433	dry N + NO	13·5 c.c.	22·5°	528 mm.
		„ N......	13·5 „	22·5	521 „

	Calculated for $C_{28}H_{22}N_2O$.		Found.		
			I.	II.	III.
C_{28}......	336	83·58	83·39	83·38	—
H_{22}......	22	5·47	5·79	5·65	—
N_2......	28	6·97	—	—	7·54
O.......	16	3·98	—	—	—
	402	100·00			

The alcoholic solution (*a*), poured off from the yellow oil, was concentrated, and allowed to stand for some days. It deposited a yellow crystalline substance, which, after recrystallising twice from hot alcohol, formed stellate groups of colourless, slender needles melting constantly at 206°.

Analysis of the compound dried at 100° gave figures agreeing with the formula $C_{21}H_{16}N_2$:—

	Substance.	CO_2.	H_2O.
I........	0·2254	0·7005	0·1115

	Substance.		*v.*	*t.*	*p.*
III....	0·1433	dry N + NO	13·5 c.c.	23°	445 mm.
		„ N......	13·5 „	23	421 „

	Calculated for $C_{21}H_{16}N_2$.		Found.	
			I.	II.
C_{21}........	252	85·13	84·75	—
H_{16}........	16	5·41	5·49	—
N_2........	28	9·46	—	9·93
	296	100·00		

We have already given reasons for regarding this compound as either 1-3-4- or 1-4-5-*triphenylpyrazole* (*v. supra*). Ignoring intermediate stages, the reaction may be expressed by the equation

$$C_{22}H_{16}O_2 + C_6H_5{\cdot}NH{\cdot}NH_2 = C_{21}H_{16}N_2 + C_6H_5{\cdot}CHO + H_2O.$$

Action of Hydroxylamine on Dibenzoylcinnamene.

Equal weights of dibenzoylcinnamene and hydroxylamine hydrochloride were heated in alcoholic solution in a sealed tube at 150° for about six hours. There was pressure in the tube, and a gas was given off which burned with a green-edged flame (ethyl chloride). Water precipitated an oil, which partially solidified on standing; this was extracted with ether, which on evaporation left it as an oil which showed no tendency to solidify. It was, therefore, dissolved in light petroleum (b. p. 50—60°); the solution was allowed to stand for half an hour, so as to deposit a dark oil, and then filtered. From the filtrate a colourless substance separated, which, however, was very impure, and could only be purified by repeated recrystallisation, both from light petroleum and from methyl alcohol. It formed colourless crystals melting at 73—75°.

Analysis showed that it had the formula $C_{15}H_{11}NO$:—

	Substance.	CO_2.	H_2O.
I........	0·2186	0·6510	0·1007
II........	0·2188	0·6525	0·1003

	Substance.		*v.*	*t.*	*p.*
III....	0·1079	dry N + NO	9·02 c.c.	17°	487 mm.
		„ N......	9·02 „	17·5	480 „
IV....	0·1383	dry N + NO	13·5 „	24	434 „
		„ N......	13·5 „	23·5	422 „

	Calculated for $C_{15}H_{11}NO$.		Found.			
			I.	II.	III.	IV.
C_{15}....	180	81·45	81·21	81·33	—	—
H_{11}....	11	4·98	5·11	5·05	—	—
N.....	14	6·33	—	—	6·28	6·34
O.....	16	7·24	—	—	—	—
	221	100·00				

The reaction, the mechanism of which has been discussed in the introduction to this paper, corresponds with that occurring in the case of phenylhydrazine, and may be expressed by the equation

$$C_{22}H_{16}O_2 + NH_2{\cdot}OH = C_{15}H_{11}NO + C_6H_5{\cdot}CHO + H_2O.$$

It might possibly be expected that the benzaldehyde liberated in this reaction would react with the excess of hydroxylamine to form benzaldoxime. No benzaldoxime, however, could be detected; but, on the other hand, benzoic acid had been formed in considerable quantity. This is, however, in harmony with what Beckmann (*Ber.*, 22, 437) has observed concerning the behaviour of benzaldehyde with hydroxylamine hydrochloride under conditions resembling those of our experiment. He finds that they react according to the equation

$$C_6H_5{\cdot}CHO + NH_2{\cdot}OH,HCl = C_6H_5{\cdot}COOH + NH_4Cl.$$

Action of Bromine on Dibenzoylcinnamene.

The behaviour of dibenzoylcinnamene towards bromine was studied by Japp and Miller (Trans., 1885, 36). They obtained an unstable additive compound, a bromine determination of which gave figures "somewhat too high for a *tetra*bromide." The compound was found to lose bromine when exposed to air.

We have re-examined this compound and find, as the result of complete analyses of different preparations, that it has the empirical formula of a *pentabromide*. The rapidity with which the compound loses bromine (*v. infra*), and the fact that Japp and Miller left the *powdered* substance for two hours over sulphuric acid before analysing it, amply account for the deficit in their bromine determination (52·00 instead of 56·18 Br per cent.).

10 grams of dibenzoylcinnamene were dissolved in the smallest possible quantity of dry chloroform, 10 grams of dry bromine were added, and the flask was closed with a perforated stopper through which a sulphuric acid tube passed. After standing for two days, the liquid had deposited the additive compound in large, ruby-red plates. These were washed with a little chloroform, dried by brief exposure to the air *without powdering*, and analysed at once.

	Substance.	CO_2.	H_2O.
I........	0·2561	0·3527	0·0568
II........	0·2299	0·3163	0·0511

III. 0·3554 gram gave 0·4622 gram AgBr (Carius).

	Calculated for $C_{22}H_{16}O_2,Br_5$.		Found.		
			I.	II.	III.
C_{22}	264	37·08	37·55	37·52	—
H_{16}	16	2·25	2·46	2·47	—
O_2	32	4·49	—	—	—
Br_5	400	56·18	—	—	55·31
	712	100·00			

Also, 0·5797 gram, weighed out at the same time as the foregoing, and exposed for six days in a vacuum-desiccator over soda-lime in the dark, lost 0·3208 gram, after which the weight remained constant. This corresponds with 55·34 per cent. of bromine, agreeing with the Carius determination. The residue had the melting point of dibenzoylcinnamene.

Another portion was exposed to the air for from five to six hours, after which the bromine was determined by Carius's method. It was found to have lost over 10 per cent. of bromine.

Boiling the pentabromide with alcohol instantly removes the whole of the bromine; the substance dissolves, and the solution, on cooling, deposits pure dibenzoylcinnamene.

On heating the substance alone in a test-tube, it is decomposed, giving off bromine and hydrobromic acid. The residue, recrystallised from acetic acid, formed white needles melting at 170°, which looked homogeneous; but the percentage of bromine (39·93 per cent.) showed that the substance was a mixture. It was not further examined.

In spite of the perfectly definite and homogeneous appearance of this "pentabromide," and in spite of the fact that a second preparation gave figures practically identical with the foregoing, we are inclined to regard this substance as an isomorphous mixture of a lower and a higher bromide—possibly of a dibromide with a hexabromide—and to consider that the approximation of the composition to that of a pentabromide is a mere coincidence. Thus the chloroform mother liquors from the "pentabromide" deposited crystals absolutely indistinguishable in appearance from the "pentabromide," but containing less bromine. In one preparation, this second crop contained 54·00 per cent. of bromine; in another preparation, two bromine determinations of the second crop gave only 37·95 and 37·89 per cent. respectively—numbers which are only about 4 per cent. higher than that required by a dibromide.

Unless moisture is rigidly excluded during the preparation, substitution occurs at the same time. Thus in one preparation, in which the before-described precautions were neglected, the red crystals of of the additive compound were mixed with yellow crystals of a second compound. By treating the mixture with boiling alcohol the additive compound was removed, after which the yellow compound was recrystallised from a large bulk of boiling glacial acetic acid, in which it is only sparingly soluble. It was deposited in small, colourless crystals melting at 198°. It is practically insoluble in boiling alcohol.

Analysis gave figures agreeing with the formula $C_{22}H_{13}Br_3O$:—

	Substance.	CO_2.	H_2O.
I........	0·2852	0·5162	0·0665
II........	0·2111	0·3849	0·0490

III. 6·5149 gram gave 0·5376 AgBr (Carius).

	Calculated for $C_{22}H_{13}Br_3O$.		Found.		
			I.	II.	III.
C_{22}......	264	49·53	49·36	49·72	—
H_{13}......	13	2·44	2·59	2·58	—
Br_3......	240	45·03	—	—	44·41
O.......	16	3·00	—	—	—
	533	100·00			

This would be the formula of a *tribromotriphenylfurfuran*, the formation of which might be accounted for by the following equations :—

(1.) $C_{22}H_{16}O_2 + 4Br = C_{22}H_{14}Br_2O_2 + 2HBr$;

Dibromodibenzoylcinnamene.
(Hypothetical intermediate compound.)

(2.) $C_{22}H_{14}Br_2O_2 + HBr = C_{22}H_{13}Br_3O + H_2O$,

Tribromotriphenylfurfuran.

the last reaction corresponding with the formation of triphenylchlorofurfuran from dibenzoylcinnamene and hydrochloric acid (*v. supra*).

Some of the reactions here described have also been studied in the lepiden series by one of us in conjunction with Dr. Laycock, and will form the subject of a separate paper.

Normal School of Science,
South Kensington.

XLIX.—*Crystallographical Relations of the Derivatives of Dibenzoylcinnamene.*

By ALFRED E. TUTTON, Assoc. N.S.S., Demonstrator in Chemistry at the Normal School of Science, South Kensington.

IN this paper are presented the results of the crystallographical examination of several of the new compounds described by Drs. Japp and Klingemann in the preceding communication. Eleven well-crystallising substances derived from dibenzoylcinnamene have been examined, and several interesting relations between their symmetry discovered which may be of use in further elucidating the question of the general relation between crystalline form and chemical composition.

The substances investigated were:—

Dibenzoylcinnamene itself;
Triphenylcrotolactone, isomeric with dibenzoylcinnamene;
Dibenzoylcinnamenimide;
Triphenylpyrrholone, the imide of triphenylcrotolactone;
Methyl-, ethyl-, propyl-, and allyl-derivatives of triphenylpyrrholone;
Bromine-derivatives of methyl and ethyl triphenylpyrrholone;
A compound of the composition $C_{21}H_{16}O$.

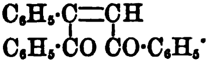
The main interest of the work lies in the isomorphous and morphotropic relations observed between the alkyl-derivatives of triphenylpyrrholone. The addition of a CH_2 group is found, in the particular cases examined, to be accompanied by a very slight alteration in the axial ratios without any disturbance of the crystallographic symmetry, similar to that which occurs when metals of the same chemical family are substituted for one another in their salts. The problem has been somewhat complicated by the prevalence of polymorphism, several of the alkyl-derivatives being found in two and probably even three distinct forms.

A remarkable case of dispersion of optic axes for different colours of the spectrum has been found in case of the monoclinic variety of ethyl triphenylpyrrholone. Between the red and the green the dispersion amounts to more than 54°, and is accompanied by a crossing of the optic axial planes. Consequently the interference figure in white light is exceptionally complicated, somewhat resembling the well-known one of brookite in the rhombic system.

The paper is concluded by the results of an investigation as to the identity or otherwise of the oxylepidenic and isoxylepidenic acids described by Zinin. In the preceding paper the two substances have been shown to be probably identical from chemical considerations; their crystalline forms are now shown to be identical.

The goniometrical measurements have been made with the large horizontal circle goniometer supplied by Fuess, of Berlin, which reads accurately to half a minute of arc. The optic axial measurements were made with the universal apparatus described by Professor Groth and constructed by Fuess, and the determinations of extinctions were made by means of a polarising microscope constructed for the author by Swift.

αβ-Dibenzoylcinnamene,



$$\begin{array}{ll} C_6H_5{\cdot}C & = CH \\ \quad | & \quad | \\ C_6H_5{\cdot}CO & CO{\cdot}C_6H_5 \end{array}$$

Melting point 129°. Crystallised from a mixture of chloroform and carbon bisulphide.

This compound was obtained five years ago by Japp and Miller (Trans., 1885, 35), and forms the stock material from which the ten following substances are derived.

An improved method of preparation from benzil, acetophenone, and alcoholic potash is given in Part II of the preceding paper.

The specimen examined consisted of very small, slightly yellow prisms; the largest observed were about 2 mm. long and $\frac{3}{4}$ mm. thick. They were generally very much striated and distorted, and the reflections were consequently not good. They were much aggregated, several parallel crystals frequently growing together.

System: rhombic. Habit: prismatic.

Ratio of axes: $a : b : c = 0{\cdot}6898 : 1 : 0{\cdot}6500$.

Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $p = \{110\}\infty P$; $p' = \{130\}\infty\breve{P}3$; $m = \{101\}\bar{P}\infty$; $r = \{112\}\frac{1}{2}P$.

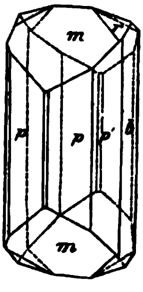


FIG. 1.

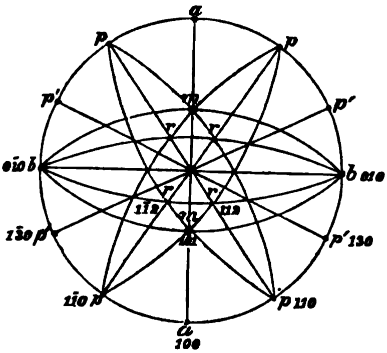


FIG. 2.

The prism faces were best developed. Of the end faces, the macrodome $m(101)$ was most prominent. The pyramid faces $r(112)$ were generally present, but small. The macropinacoid $a(100)$ was only observed on one crystal.

A typical crystal is represented in Fig. 1 and its spherical projection in Fig. 2.

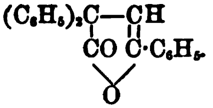
The following goniometrical measurements were obtained :—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
bp = 010 : 110	12	54° 25′—57° 28′	55° 24′	*
bp' = 010 : 130	4	25 21—26 14	25 47	25° 47′
$p'p$ = 130 : 110	2	29 32—29 35	29 33	29 37
pm = 110 : 101	6	54 33—56 8	55 39	55 38
mr = 101 : $1\bar{1}2$	2	24 0—24 4	24 2	24 12
br = 010 : 112	2	73 36—73 38	73 37	*
pr = 110 : 112	4	60 10—60 25	60 19	60 13
am = 100 : 101	—	—	—	46 42
bm = 010 : 101	6	88 31—91 47	90 0	—

The angles marked with an asterisk were used as basis of the calculations.

The plane of the optic axes is the brachypinacoid $b(010)$. A section cut parallel to the basal plane showed both axes, which in castor oil appeared separated 104° 50′ for sodium light. Sections parallel to $a(100)$ were not possible owing to thinness and friability of the prisms. The dispersion was not large, for readings with lithium and thallium light were almost identical with those obtained with sodium light. The hyperbolic brushes were bordered with blue outside and red inside.

Triphenylcrotolactone,



This compound is isomeric with dibenzoylcinnamene and is prepared from the latter substance by heating it for half an hour at 310° (in diphenylamine vapour); on extracting with boiling alcohol and allowing the alcoholic solution to stand, well formed crystals are deposited.

Melting point 117—118°; recrystallised from alcohol.

Triphenylcrotolactone is totally different from its isomeride dibenzoylcinnamene. It forms brilliant, colourless prisms averaging 2—6 mm. in length and ½ mm. in thickness. The prism zone is very nearly tetragonal in apparent habitus, the angles being almost exactly 45°; but the principal end face, which is frequently the only other plane developed besides the prism faces, is inclined 81° 32′ to the vertical axis. The crystals, moreover, are biaxial, and the optical properties indicate the presence of only one plane of symmetry. The disposition of the other faces exhibited by many of the crystals also points to mono-symmetry. The result of a large number of measurements of the prism zone shows that the angle between *a* and *p* is slightly less, and that between *p* and *b* slightly greater than 45°. Thus out of 40 measurements of *ap*, 34 were less than 45°, and of 32 measurements of *pb*, 31 were greater than 45°. The crystals are therefore monoclinic, with a prism zone of nearly 45°.

System: monoclinic. Habit: prismatic. $\beta = 81° 32'$.
Ratio of axes: $a : b : c = 1{\cdot}0029 : 1 : 1{\cdot}0711$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $c = \{001\}oP$; $p = \{110\}\infty P$; $m = \{011\}\breve{P}\infty$; $q = \{012\}\frac{1}{2}\breve{P}\infty$; $n = \{\bar{1}12\} + \frac{1}{2}P$; $o = \{\bar{1}11\} + P$; $s = \{\bar{1}02\} + \frac{1}{2}\bar{P}\infty$; $r = \{102\} - \frac{1}{2}\bar{P}\infty$.

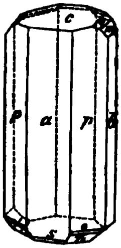


Fig. 3.

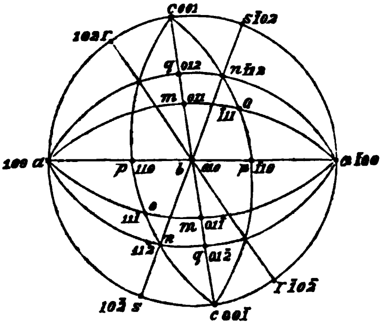


Fig. 4.

Fig. 3 shows the general appearance of an average crystal, and Fig. 4 represents its spherical projection.

The prism faces $p\{110\}$ were best developed and gave good reflections. The orthopinacoid $a\{100\}$ was always found, but generally gave more distorted reflections. The clinopinacoid $b\{010\}$ was generally very narrow, often a mere line. The basal plane $c\{001\}$ was always well developed and gave excellent reflections. The clinodome $m\{011\}$ and the hemi-pyramid $n\{\bar{1}12\}$ were not always developed, but when present, gave reliable reflections. The planes of $q\{012\}$ and $o\{\bar{1}11\}$ were generally very small and reflections faint. Traces only of $r\{102\}$ were found, the reflections being too distorted for accurate orientation.

The following measurements were obtained:—

Angle observed.	No. of measurements.	Limits.	Mean observed.	Calculated.
$ap = 100 : 110$	40	44° 10′—45° 36′	44° 47′	*
$pb = 110 : 010$	32	44 49—45 48	45 13	*
$ac = 100 : 001$	19	80 52—81 49	81 29	81° 32′
$cs = 001 : \bar{1}02$	3	29 38—30 21	29 55	29 51
$sa = \bar{1}02 : \bar{1}00$	2	68 17—68 53	68 35	68 37
$am = 100 : 011$	19	83 31—85 0	84 13	84 12
$mo = 011 : \bar{1}11$	5	37 56—38 13	38 7	38 14
$oa = \bar{1}11 : \bar{1}00$	6	57 31—57 54	57 43	57 34
$aq = 100 : 012$	1	—	82 35	82 32
$qn = 012 : \bar{1}12$	1	—	26 20	26 20
$na = \bar{1}12 : \bar{1}00$	17	70 34—71 23	71 2	70 58
$bm = 010 : 011$	20	43 7—43 33	43 19	*
$mq = 011 : 012$	1	—	18 49	18 45
$mc = 011 : 001$	22	46 32—47 6	46 40	46 41
$qc = 012 : 001$	2	27 43—28 0	27 52	27 56
$bn = 010 : \bar{1}12$	5	63 20—63 38	63 28	63 29
$ns = \bar{1}12 : \bar{1}02$	2	26 16—26 42	26 29	26 31
$cp = 001 : 110$	38	83 32—84 28	84 0	*
$po = 110 : 11\bar{1}$	13	35 14—35 43	35 25	35 22
$on = 11\bar{1} : 11\bar{2}$	9	21 19—21 34	21 27	21 32
$nc = 11\bar{2} : 00\bar{1}$	23	38 51—39 9	39 0	39 6
$bo = 010 : \bar{1}11$	2	51 43—51 58	51 51	51 54
$oo = \bar{1}11 : \bar{1}\bar{1}1$	1	—	76 19	76 12

In parallel light with crossed Nicols, the extinction upon the orthopinacoid *a*(100) is parallel to the prism edges. The extinction upon the symmetry plane *b*(010) makes an angle of 21—22° with the vertical axis or prism edges. In convergent light a brush is seen through the orthopinacoid, the optic axis corresponding being just outside the field in the direction of *r* or *c*. When the crystal is placed so that the edges of the orthopinacoid with the prism and basal plane are parallel to the directions of the crossed Nicols, the brush appears to lie along a diameter of the field parallel with the vertical axis of the crystal, that is, parallel to the prism edges. The plane of symmetry *b*(010) is therefore the plane of the optic axes.

Dibenzoylcinnamenimide, $C_{23}H_{17}NO$.

Melting point 180°.

This substance is deposited when an excess of strong alcoholic ammonia is added to a hot solution of dibenzoylcinnamene in alcohol and the solution allowed to cool.

The crystals are colourless, lustrous tables, in some preparations taking the form of thin plates and in others of fairly thick ones, the principal face varying in size from 2 mm. by 1½ mm. to very minute.

System: rhombic. Habit: tabular.
Ratio of axes: $a : b : c = 0{\cdot}6911 : 1 : 0{\cdot}8151$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $c = \{001\}0P$; $p = \{110\}\infty P$; $p' = \{120\}\infty\breve{P}2$; $o = \{111\}P$; $n = \{121\}2\breve{P}2$; $v = \{112\}\frac{1}{2}P$; $r = \{011\}\breve{P}\infty$; $s = \{012\}\frac{1}{2}\breve{P}\infty$.

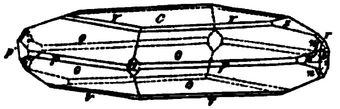


FIG. 5.

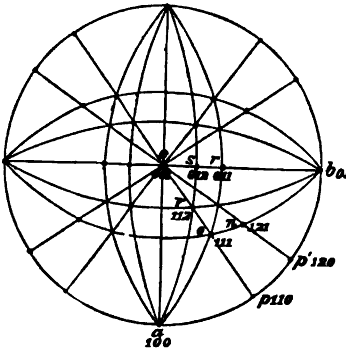


FIG. 6.

A representative crystal is shown in Fig. 5, and its spherical projection in Fig. 6.

The basal plane $c(001)$ is the best developed face, the crystals being tabular upon it. The primary pyramid $o(111)$ is always present, and frequently is the only form noticeable besides the basal plane. The other forms in the specimens examined were generally small.

The following angular measurements were obtained:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
co = 001 : 111	85	53° 31′—56° 51′	55° 7′	*
vo = 112 : 111	2	19 24—19 40	19 32	19° 28′
op = 111 : 110	2	34 22—35 1	34 42	34 53
oo = 111 : 11$\bar{1}$	41	68 7—70 58	69 47	69 46
bn = 010 : 121	4	43 19—44 29	43 37	43 29
bo = 010 : 111	54	61 2—63 50	62 12	*
oo = 111 : 1$\bar{1}$1	29	54 28—56 56	55 35	55 36
oo = 111 : $\bar{1}$11	24	84 15—86 18	84 50	84 52
or = 111 : 011	3	42 7—43 9	42 28	42 26
oo = $\bar{1}$11 : $\bar{1}\bar{1}\bar{1}$	24	93 52—95 45	95 10	95 8
oa = 111 : 100	2	47 10—48 7	47 38	47 34
bs = 010 : 012	2	67 30—67 58	67 44	67 49
sc = 012 : 001	2	21 59—22 20	22 9	22 11
bp′ = 010 : 120	3	35 40—35 44	35 42	35 53

The extinctions upon the basal plane $c(001)$ in parallel polarised light are parallel to the crystallographic axes.

The plane of the optic axes is the brachypinacoid $b(010)$. A thin crystal, that is, a thin plate parallel to $c(001)$, shows in convergent light both axes when immersed in oil. The angle is very large and invisible in air. This is the obtuse angle; hence the vertical axis is the second median line. A section was obtained with some difficulty, owing to general thinness of plates, parallel to $a(100)$ and perpendicular to the first median line. This section, which required to be cut very thin, showed in oil the axes and rings separated at their acute angle. The following measurements of the acute and obtuse apparent optic axial angles in oil were obtained, using sodium light:—

	Acute angle $2Ha$.		Obtuse angle $2Ho$.
	98° 25′		118° 48′
	98 29		118 26
	98 19		118 55
	—		119 5
Mean	98 24	Mean	118 48

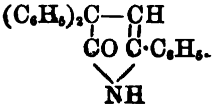
Calculated by the formula

$$\tan Va = \frac{\sin Ha}{\sin Ho},$$

the true angle $2Va$ of the optic axes is 82° 40′.

The dispersion is very small, and appears to be of the nature $\rho < v$.

Triphenylpyrrholone or 3-Diphenyl-5-phenylpyrrholone, the Imide of Triphenylcrotolactone,



$$\begin{array}{c} (C_6H_5)_2C{-}CH \\ CO \quad C{\cdot}C_6H_5. \\ NH \end{array}$$

This substance is isomeric with the dibenzoylcinnamenimide just described. The latter substance is readily transformed into triphenylpyrrholone by heating it to its melting point (180°), when it rapidly resolidifies again, owing to the isomeric change.

Melting point 221°. Crystallised from ether.

Colourless prisms, generally very small and much distorted and striated, varying in size from the finest needles, 1—2 mm. long, to prisms of ½ mm. thickness.

System: triclinic. Habit: prismatic.

Axial angles: $\alpha = 78° 56'$; $\beta = 73° 23'$; $\gamma = 87° 82'$.

Ratio of axes: $a : b : c = 0{\cdot}7791 : 1 : 0{\cdot}5124$.

Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $p = \{110\}\infty P'_{|}$; $p' = \{1\bar{1}0\}\infty'_{|}P$; $m = \{011\}_{|}\breve{P}'\infty$; $n = \{0\bar{1}1\}'\breve{P}_{|}\infty$; $r = \{101\}'\bar{P}'\infty$; $s = \{\bar{1}01\}_{|}\bar{P}_{|}\infty$.

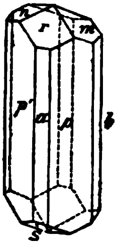


FIG. 7.

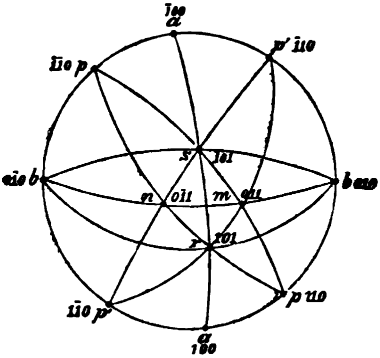


FIG. 8.

Fig. 7 represents a typical crystal, and Fig. 8 its spherical projection.

The prism faces p' are best developed. The brachypinacoid b is also generally very prominent, and the prism p usually present, but the macropinacoid a is in most crystals either very narrow or entirely absent. The four pairs of domes are, as a rule, equally developed.

Owing to distortion, the reflections were considerably below the average of those of the other compounds described in this communication; hence the difference between the observed and calculated values of the angles is also somewhat greater.

The following measurements were made :—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
$bp = 010 : 110$	21	48° 12′—49° 23′	48° 59′	*
$pa = 110 : 100$	2	35 3—35 9	35 6	35° 2′
$ap' = 100 : 1\bar{1}0$	3	39 13—39 14	39 14	39 24
$pp' = 110 : 1\bar{1}0$	22	73 54—75 35	74 26	*
$p'b = 1\bar{1}0 : 0\bar{1}0$	21	56 1—57 18	56 38	56 35
$bm = 010 : 011$	15	53 26—54 51	54 14	54 12
$mn = 011 : 0\bar{1}1$	10	51 13—51 25	51 17	51 43
$nb = 0\bar{1}1 : 0\bar{1}0$	10	73 37—74 58	74 24	74 5
$br = 010 : 101$	10	77 10—78 22	78 1	77 56
$bs = 010 : \bar{1}01$	3	81 0—82 6	81 40	81 45
$pm = 110 : 011$	16	55 31—56 32	56 5	56 2
$ms = 011 : \bar{1}01$	14	43 34—45 19	43 52	44 7
$sp = \bar{1}01 : \bar{1}\bar{1}0$	14	78 20—80 34	80 4	79 51

Angle measured	No. of measurements.	Limits.	Mean observed.	Calculated.
$pr = 110 : 101$	15	48 26—49 55	49 6	*
$rn = 101 : 0\bar{1}1$	11	38 50—39 22	39 2	39 20
$np = 0\bar{1}1 : \bar{1}\bar{1}0$	10	91 10—92 9	91 51	91 34
$ar = 100 : 101$	5	44 42—45 24	45 11	45 13
$rs = 101 : \bar{1}01$	8	64 25—65 29	64 38	64 45
$sa = \bar{1}01 : \bar{1}00$	3	70 3—70 15	70 7	70 2
$p'r = 1\bar{1}0 : 101$	18	62 6—62 57	62 45	*
$rm = 101 : 011$	17	34 20—34 55	34 38	*
$mp' = 011 : \bar{1}10$	20	81 53—83 19	82 31	82 37
$p'n = 1\bar{1}0 : 0\bar{1}1$	13	67 22—68 20	67 51	67 38
$ns = 0\bar{1}1 : \bar{1}01$	14	43 11—44 48	44 22	44 33
$sp' = \bar{1}01 : \bar{1}10$	14	67 1—68 31	67 39	67 49

The extinction upon *p'* makes an angle of 16—17°, and that upon *b* 4—5°, with the vertical prism edges. Owing to the minuteness and friability of the crystals, the optical properties could not be further studied.

The hydrogen in the imido-NH-group of triphenylpyrrholone is replaceable by alkyl radicles. Hence it has been possible to prepare a series of derivatives ascending by CH_2. All these derivatives are solid substances which crystallise well, and the methyl, ethyl, and propyl members have been somewhat fully investigated. The crystallographical relationships which such a series presents are of course of theoretical importance, as affording additional data towards the solution of the problem of the general relationship between chemical composition and crystalline form. Since the impetus imparted to the subject by the researches of Professor Groth upon the morphotropical relations of the derivatives of the aromatic hydrocarbons, many similar relationships have been described by other crystallographers, and it is hoped the similarities of structure met with in the present ascending series of substituted imides may form another link in the growing chain of evidence. Special thanks are due to Drs. Japp and Klingemann, who, entering fully into the subject from the crystallographical point of view, have spent much valuable time in preparing and analysing the higher members of the series, although of no further use in elucidating the chemical constitution of the fundamental imide.

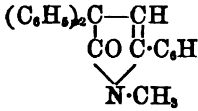
Each of the three derivatives, the methyl, ethyl, and propyl compounds, has been obtained in two distinct forms. These substances are, therefore, at least dimorphous. It is probable, indeed, that two of them, and possibly all three, are even trimorphous, but the third varieties have not been obtained in crystals sufficiently well formed for measurement. That the production of different forms is owing to polymorphism, and not to chemical isomerism, is shown by the fact that one variety may be obtained from the other by simply altering the conditions of crystallisation from the same solvent. Their identical chemical composition was established by direct analysis. Both varieties also furnish the same bromine-derivatives.

The methyl-derivative has been obtained in hexagonal plates and in triclinic prisms. The ethyl compound has been obtained in triclinic prisms exactly resembling those of the methyl compound in habit and disposition of faces; moreover, the angles are so near those of the latter compound that one might infer the existence of true and complete isomorphism. Besides the triclinic form, the ethyl-derivative has also been obtained in monoclinic crystals. Of the two forms of the propyl compound, one is monoclinic and resembles the monoclinic form of the ethyl compound as closely as the triclinic form of the latter substance resembles that of the methyl compound. There are exactly the same faces developed according to the same habit, the only difference being the slight alteration in the angles. This is not only true of particular zones, but of every zone of the two compounds. The similarity in the optical properties of the monoclinic ethyl- and propyl-derivatives is also very striking, inasmuch as both are compounds of high dispersion. In the case of the propyl-derivative, the difference between the apparent angle of the optic axes for lithium and thallium light amounts to 11°. In the case of the ethyl-derivative, this difference is increased to such an extent that it affords a remarkable example of a case of crossed axial planes; the optic axial plane is perpendicular to the symmetry plane, as in the propyl-derivative, for lithium and sodium light, and then crosses to a plane at right angles for thallium light, the total dispersion amounting to 54°.

The second form of the propyl compound belongs to the rhombic system, and it may be remarked that a similar rhombic form of the ethyl compound was once obtained, but, unfortunately, lost on attempting to recrystallise, as the monoclinic form separated out and the rhombic form was never again obtained.

Thus apparently isomorphous relations are found between the triclinic forms of the methyl- and ethyl-derivatives and the monoclinic forms of the ethyl- and propyl-derivatives. Morphotropic relations of almost as complete a nature have also been observed between the monoclinic forms of the ethyl- and propyl-derivatives on the one hand, and the allyl-derivative upon the other.

Methyl Triphenylpyrrholone, or 1-Methyl-3-diphenyl-5-phenylpyrrholone,



This substance crystallises in two forms, as already indicated. As ordinarily prepared, by acting upon a hot alcoholic solution of dibenzoylcinnamene with alcoholic methylamine, it is deposited on cooling in triclinic prisms. When these crystals are heated to 340° for an hour, or distilled under reduced pressure, and the product crystallised from alcohol, the crystals obtained belong to the rhombohedral-hexagonal system. The latter form is also obtained along with the triclinic when the preparation from alcoholic dibenzoylcinnamene and methylamine is conducted in a weaker solution and below 40°. Both forms yield the same bromine-derivative, identical both chemically and crystallographically.

Triclinic Variety.

Melting point 143°. Obtained as above by deposition from the hot alcoholic solution. The crystals are extremely small, longest dimension about 0·7 mm., but well formed and very brilliant, yielding excellent reflections. Larger crystals of the same form are obtained upon recrystallisation from carbon bisulphide, but these are too much distorted for accurate measurement.

Axial angles: $\alpha = 79° 52'$; $\beta = 86° 3'$; $\gamma = 70° 26'$.
Ratio of axes: $a : b : c : = 0·9059 : 1 : 0·8695$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $c = \{001\}oP$;
$p = \{1\bar{1}0\}\infty{}_{|}'P$; $o = \{111\}P'$; $r = \{1\bar{1}1\}'P$; $o' = \{\bar{1}11\}{}_{,}P$;
$s = \{\bar{1}\bar{1}1\}P_{,}$; $r' = \{1\bar{1}2\}\frac{1}{2}'P$; $m = \{101\}'\bar{P}'\infty$; $m = \{\bar{1}01\}{}_{,}\bar{P}_{,}$;
$k = \{011\}{}_{,}\breve{P}'\infty$; $q = \{0\bar{1}1\}'\breve{P}_{,}\infty$.

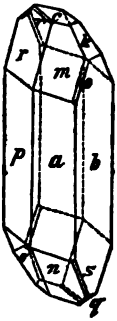


FIG. 9.

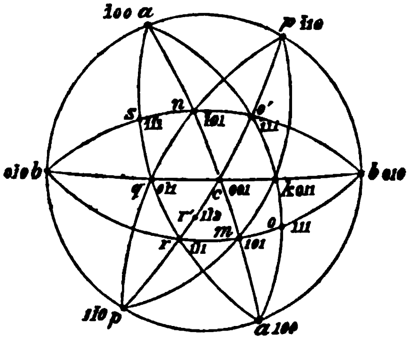


FIG. 10.

The general appearance of the crystals is seen in Fig. 9, and the spherical projection in Fig. 10.

The brachypinacoid $b(010)$ is best developed, and frequently the crystals are tabular upon it. The macropinacoid $a(100)$ is generally well formed, as is frequently the case also with the hemi-prism $p(1\bar{1}0)$; the latter, however, is sometimes a mere line, the two pinacoids being the predominating planes. Of the hemi-pyramids and domes, $r(1\bar{1}1)$, $o'(\bar{1}11)$, $m(101)$, and $n(\bar{1}01)$ are always present; $q(0\bar{1}1)$, as a rule, is also present, but not so fully developed as the four end forms just mentioned. Every preparation does not exhibit the basal plane $c(001)$ and the hemi-dome $k(011)$, but in certain preparations they were found well developed; $r'(1\bar{1}2)$ was only noticed in one preparation, and $o(111)$ and $s(\bar{1}\bar{1}1)$ only upon one crystal, and the images were then too striated for use.

The following measurements were obtained:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
$ba = 100 : 100$	19	68° 56′—69° 53′	69° 19′	*
$ap = 100 : 1\bar{1}0$	19	51 15—52 8	51 47	—
$pb = 1\bar{1}0 : 0\bar{1}0$	19	58 15—59 20	58 54	*
$bm = 010 : 101$	23	67 25—68 50	68 1	*
$mr = 101 : 1\bar{1}1$	24	35 51—36 42	36 13	—
$rb = 1\bar{1}1 : 0\bar{1}0$	23	75 7—76 19	75 46	*
$bo' = 010 : \bar{1}11$	16	58 51—59 46	59 12	59° 19′
$o'n = \bar{1}11 : \bar{1}01$	20	36 36—37 24	36 57	36 55
$nb = \bar{1}01 : 0\bar{1}0$	20	83 39—84 9	83 49	83 46
$bk = 010 : 011$	1	—	40 47	40 47
$kc = 011 : 001$	1	—	36 59	36 37
$cq = 001 : 0\bar{1}1$	1	—	48 11	48 11
$qb = 0\bar{1}1 : 0\bar{1}0$	9	53 58—54 17	54 9	54 3
$am = 100 : 101$	12	40 50—41 22	41 2	40 59
$mc = 101 : 001$	1	—	41 5	41 8
$mn = 101 : \bar{1}01$	11	90 0—90 18	90 11	90 9
$cn = 001 : \bar{1}01$	1	—	49 4	49 3
$na = \bar{1}01 : \bar{1}00$	10	48 36—49 3	48 49	48 52
$ar = 100 : 1\bar{1}1$	11	55 28—55 56	55 36	55 41
$rq = 1\bar{1}1 : 0\bar{1}1$	10	43 18—43 26	43 23	43 17
$qa = 0\bar{1}1 : \bar{1}00$	10	80 48—81 8	81 1	81 2
$ao' = \bar{1}00 : \bar{1}11$	8	69 11—69 19	69 16	69 10
$pm = 1\bar{1}0 : 101$	11	67 40—68 10	67 56	67 53
$pr = 1\bar{1}0 : 1\bar{1}1$	18	43 22—44 0	43 44	*
$rr' = 1\bar{1}1 : 1\bar{1}2$	1	—	19 51	19 55
$r'c = 1\bar{1}2 : 001$	1	—	29 23	29 20
$ro' = 1\bar{1}1 : \bar{1}11$	16	95 0—95 46	95 16	95 13
$o'p = \bar{1}11 : \bar{1}10$	14	40 44—41 20	40 59	41 3
$pq = 1\bar{1}0 : 0\bar{1}1$	14	69 10—69 46	69 29	69 27
$qn = 0\bar{1}1 : \bar{1}01$	14	51 10—51 26	51 20	51 17
$np = \bar{1}01 : \bar{1}10$	18	58 57—59 39	59 13	59 16

There are three cleavages parallel to the two pinacoids and the basal plane. The direction of extinction upon the brachypinacoid $b(010)$ makes an angle of about 33° with the vertical axial edge. The extinction upon the macropinacoid $a(100)$ occurs at an angle of about 8° with the vertical edge (ab). In convergent light, an optic axis and its system of rings is seen on looking through a cleavage plate or a thin crystal parallel to $a(100)$ towards the left-hand corner of the field nearest the observer.

Rhombohedral-Hexagonal Variety.

Melting point 138°. Crystallised three times from alcohol.

The specimens examined were yellowish-brown in colour, generally tabular upon the basal plane, but also frequently fairly thick and occasionally equally developed. The tabular crystals varied in size from exceedingly small to hexagons of a centimetre or more in diameter. The edges were modified by two complementary + and − rhombohedra, which might be considered as faces of a hexagonal pyramid. The substance is undoubtedly rhombohedral, for occasionally very perfect single rhombohedrons, exhibiting no other faces but the basal plane, were found. Also, in nearly all the thicker crystals one rhombohedron was much more prominently developed than the other, which, as a rule, merely occurred as scarcely perceptible truncations, as shown in Fig. 12. Crystals were, however, also found in which all the faces were exhibited equally, as if holohedral. One crystal in particular, shown in Fig. 11, exactly resembled the common form of sapphire, consisting of basal plane and hexagonal prism, with a series of hexagonal pyramids or complementary rhombohedra between, forming a kind of curved cone of hexagonal section. The spherical projection is shown in Fig. 14.

FIG. 11.

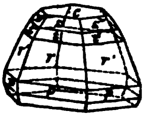
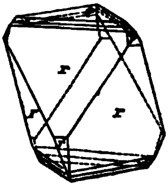


FIG. 12.



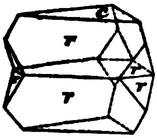


FIG. 13

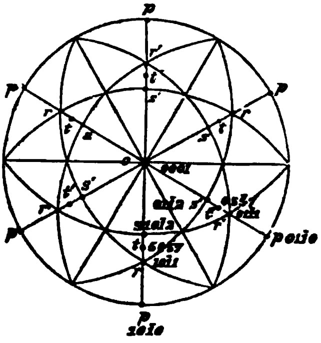


FIG. 14.

Looking through the basal plane in convergent light, the uniaxial interference figure, consisting of rectangular cross and circular rings, is well seen.

The principal rhombohedron was considered as $(10\bar{1}1)$.
Ratio of axes: $a : c = 1 : 2{\cdot}4343$.
Angle of rhombohedron: 109° 22′.

The following forms were observed:—

Form observed.	Symbol according to		
	Bravais-Miller notation.	Millerian rhombohedral notation.	Naumannian notation.
Basal plane c	(0001)	(111)	oR
Hexagonal proto-prism p	$(10\bar{1}0)$	$(11\bar{2})$	∞R
Primary + rhombohedron r	$\kappa(10\bar{1}1)$	(100)	$+R$
" − rhombohedron r'	$\kappa(01\bar{1}1)$	$(22\bar{1})$	$-R$
+ Rhombohedron s	$\kappa(10\bar{1}2)$	(411)	$+\frac{1}{2}R$
− Rhombohedron s'	$\kappa(01\bar{1}2)$	(110)	$-\frac{1}{2}R$
+ Rhombohedron t	$\kappa(5057)$	$(17, 2, 2)$	$+\frac{5}{7}R$
− Rhombohedron t'	$\kappa(0557)$	$(44\bar{1})$	$-\frac{5}{7}R$

The following angular measurements were obtained:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
$cr = 0001 : 10\bar{1}1$	39	70° 2′ — 70° 48′	70° 25′	*
$rr = 10\bar{1}1 : 10\bar{1}\bar{1}$	4	38 33 — 40 1	39 14	39° 10′
$cs = 0001 : 10\bar{1}2$	7	53 31 — 55 7	54 38	54 34
$ct = 0001 : 5057$	5	62 35 — 64 40	63 23	63 31
$rr = 10\bar{1}1 : \bar{1}101$	12	109 8 — 109 45	109 26	109 22
$rr = 10\bar{1}1 : 1\bar{1}0\bar{1}$	12	70 12 — 70 48	70 34	70 38
$pp = 10\bar{1}0 : 01\bar{1}0$	5	59 57 — 60 3	60 0	*

The basal plane c is always well developed, and in tabular crystals predominates. The primary rhombohedra r and r' predominate in thick crystals, sometimes one alone being found with basal plane. The rhombohedra s and t are generally small. Frequently a whole series of images are seen between s and r, as if from vicinal faces. Hence the curvature of the faces. The prism faces are only occasionally found, but when present give good reflections.

The crystals are frequently found twinned upon the basal plane. A characteristic twin of this description is shown in Fig. 13.

There is a good cleavage parallel to the primary rhombohedron $(10\bar{1}1)$.

The double refraction, which was determined by means of a quarter undulation mica plate, is negative.

Bromine-derivative of Methyl Triphenylpyrrholone, $C_{23}H_{18}BrNO$.

Melting point 153°. Crystallised from carbon bisulphide.

This substance, which may be obtained in identical forms from both the triclinic and hexagonal varieties of the methylimide just described by the action of bromine in chloroform solution, crystallises from carbon bisulphide in magnificent, large prisms which are generally yellow when first crystallised but may be obtained colourless on recrystallisation. These crystals have been obtained over 2 cm. in length, and from 1 to $\frac{1}{2}$ cm. thick. The faces are beautifully perfect, and give exceptionally good reflections.

System: monoclinic. Habit: prismatic. $\beta = 88° 29'$.

Ratio of axes: $a : b : c = 1{\cdot}6549 : 1 : 1{\cdot}0430$.

Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $c = \{001\}oP$; $r = \{101\}-\bar{P}\infty$; $s = \{\bar{1}01\}+\bar{P}\infty$; $p = \{110\}\infty P$; $p' = \{210\}\infty\bar{P}2$; $q = \{011\}\breve{P}\infty$; $m = \{021\}2\breve{P}\infty$; $o = \{111\}-P$; $n = \{\bar{1}11\}+P$; $t = \{221\}-2P$; $v = \{\bar{2}21\}+2P$.

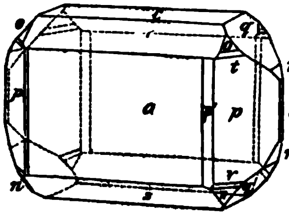


FIG. 15.

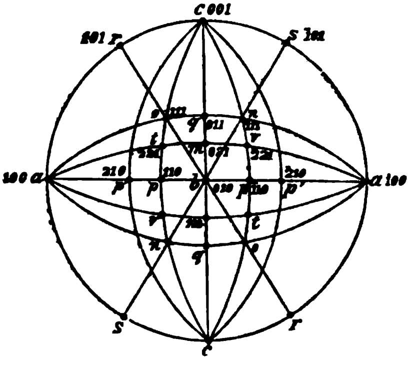


FIG. 16.

The general shape of the crystals and their spherical projection are seen in Figs. 15 and 16.

The crystals appear at first sight to be rhombic prisms, but, on measurement, the two apparently pinacoidal faces (a and c), which are generally about equally developed and the most important faces on the crystal, are found to be inclined at 88° 29′ instead of 90°. These apparently prism faces are, in fact, found on complete measurment of the substance to be the orthopinacoid and basal plane of the monoclinic system, the two ends of the crystal lying symmetrically on each side of the symmetry plane *b*, which is the zone plane of the apparent prism zone. The clinopinacoid *b*(010) at the apex of the end pyramids was only noticed once or twice, and in those instances was too rough to permit of good reflections. The orthodomes *r*(101) and *s*($\bar{1}$01) were well developed, and the prism *p*(110) and clinodome *q*(011) gave to the ends their pyramidal shape. The remaining faces were smaller, and *o*(111), *n*($\bar{1}$11), and *v*($\bar{2}$21) were so rough that their positions were only roughly determined by taking the position of their maximum illumination when viewed through the telescope arranged as a low-power microscope.

Following is a table of the angles measured:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ac = 100 : 001	15	88° 1′—88° 58′	88° 29′	*
ar = 100 : 101	11	56 18—57 0	56 42	*
cs = 001 : $\bar{1}$01	12	32 11—33 1	32 28	32° 33′
sa = $\bar{1}$01 : $\bar{1}$00	13	58 35—59 33	59 3	58 58
ap = 100 : 110	30	58 1—60 13	58 59	58 59
ap′ = 100 : 210	1	—	39 50	39 45
cq = 001 : 011	22	46 12—46 49	46 30	*
qm = 011 : 021	4	18 1—18 23	18 8	18 7
ao = 100 : 111	—	—	—	65 33
oq = 111 : 011	1	—	23 27	23 24
aq = 100 : 011	12	88 20—89 27	88 54	88 57
qa = 011 : $\bar{1}$00	11	90 42—91 36	91 6	91 3
na = $\bar{1}$11 : $\bar{1}$00	—	—	—	67 25
at = 100 : 221	8	60 32—61 52	60 55	60 51
tm = 221 : 021	1	—	28 24	28 30
ma = 021 : $\bar{1}$00	2	90 18—91 7	90 42	90 39
va = $\bar{2}$21 : $\bar{1}$00	—	—	—	61 51
co = 001 : 111	3	49 56—50 42	50 14	50 9
ot = 111 : 221	1	—	17 5	17 4
tp = 221 : 110	14	21 34—22 15	21 58	22 0
cp = 001 : 110	21	88 25—89 40	89 9	89 18
pc = 110 : 00$\bar{1}$	20	90 24—91 30	90 51	90 47
vc = 22$\bar{1}$: 00$\bar{1}$	—	—	—	68 33
nc = 11$\bar{1}$: 00$\bar{1}$	1	—	51 6	51 2
qp = 011 : 110	1	—	51 8	51 7
pq = 110 : 01$\bar{1}$	2	52 21—52 21	52 21	52 29
or = 111 : 101	1	—	41 8	41 5

There is an excellent cleavage parallel to the orthopinacoid *a*(100). The minimum of cohesion therefore lies in the symmetry plane.

In parallel polarised light, the faces perpendicular to the symmetry plane (*a*, *r*, *c*, *s*) extinguish parallel to long edges. In convergent light, the orthopinacoid a and basal plane c show only one brush. A section parallel to $s(\bar{1}01)$ shows the two axes and their system of rings separated at their acute angle and approximately in the middle of the field; the optic axial plane is perpendicular to the symmetry plane and approximately also to s. A section cut parallel to the symmetry plane $b(010)$ also showed in oil the two axes separated at their acute angle. The following measurements were obtained, using sodium light:—

	2E. Apparent acute angle in air.		2Ha. Apparent acute angle in oil.		2Ho. Apparent obtuse angle in oil.
	123° 5′		80° 20′		135° 25′
	122 45		80 55		132 40
			80 40		133 10
			80 35		
Mean..	122 55	Mean..	80 35	Mean..	133 45

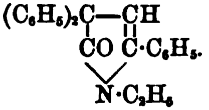
The true angle $2Va$, calculated from the formula $\tan Va = \frac{\sin Ha}{\sin Ho}$, is found to be = 70° 15′.

The mean refractive index β, calculated from the formula $\beta = \frac{\sin E}{\sin Va} = 1{\cdot}5264$.

The dispersion is very small, for the values obtained with lithium and thallium light did not differ by as much as 1° from those found for sodium light. The hyperbolic brushes were very faintly coloured, but apparently agreed with the supposition that $\rho < v$.

The sign of double refraction is positive.

Ethyl Triphenylpyrrholone,



$$\begin{array}{l}(C_6H_5)_2C{-}CH \\ \qquad\quad\ CO\ \ C{\cdot}C_6H_5. \\ \qquad\qquad N{\cdot}C_2H_5\end{array}$$

The ethyl-derivative has likewise been obtained crystallised in two forms, a triclinic and a monoclinic, by action of ethylamine upon dibenzoylcinnamene, both in alcoholic solution. The triclinic form was first obtained by using a boiling alcoholic solution of dibenzoylcinnamene, and the monoclinic by employing a weaker solution at the ordinary temperature. But it has not been found possible to determine the exact conditions under which each form is produced, sometimes one, sometimes the other, and sometimes a mixture being deposited under apparently similar conditions.

Triclinic Variety.

Melting point 123°.

These crystals resemble those of the triclinic methyl imide very closely; they exhibit most of the faces present in case of the latter compound and a few additional ones.

Axial angles: $\alpha = 78° \, 48'$. $\beta = 89° \, 10'$. $\gamma = 68° \, 2.'$
Ratio of axes: $a : b : : c = 0{\cdot}9120 : 1 : 0{\cdot}9524$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $c = \{001\}oP$;
$p = \{110\}\infty P'_{,}$; $p' = \{1\bar{1}0\}\infty_{,}'P$; $p'' = \{270\}\infty\breve{P}'_{,}\tfrac{7}{2}$; $p''' = 2\bar{1}0\}\infty_{,}'\bar{P}2$;
$m = \{101\}'\bar{P}'\infty$; $n = \{\bar{1}01\}_{,}\bar{P}_{,}\infty$; $k = \{011\}_{,}\breve{P}'\infty$; $q = \{0\bar{1}1\}'\breve{P}_{,}\infty$;
$l = \{0\bar{1}2\}\tfrac{1}{2}'\breve{P}_{,}\infty$; $r = \{1\bar{1}1\}'P$.

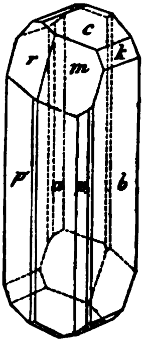


FIG. 17.

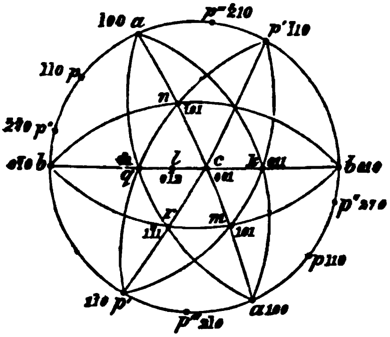


FIG. 18.

Fig. 17 shows the general appearance of the crystals, and it is interesting to compare this with the drawing of the methyl analogue (Fig. 9).

Fig. 18 is the spherical projection.

As in case of the triclinic methyl compound, the brachypinacoid *b*(010) is generally best developed. Sometimes, however, the macropinacoid *a*(100) is the most prominent. The prism face *p*′(1$\bar{1}$0) is next in importance, as it is in the triclinic methyl imide. The remaining prism faces are generally mere lines. The basal plane *c*(001) appears to be a better-developed face in this substance than in its methyl analogue, but this is really due to the fact that the forms *o*′($\bar{1}$11) and *n*($\bar{1}$01) were either not present or extremely small on the crystals examined. The faces *r*(1$\bar{1}$1), *m*(101), *k*(011) and *q*(0$\bar{1}$1) were of about the same relative importance as in case of the methyl compound.

The following angles were measured:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ab = 100 : 010	32	67° 9′—67° 55′	67° 26′	*
ap = 100 : 110	1	—	82 28	82° 19′
pb = 110 : 010	1	—	85 9	85 7
p″b = 270 : 010	1	—	14 22	14 15
ap′ = 100 : $1\bar{1}0$	31	52 41—53 27	53 10	*
p‴p′ = $2\bar{1}0$: $1\bar{1}0$	2	25 6—25 49	25 28	25 34
p′b = $1\bar{1}0$: $0\bar{1}0$	34	58 51—59 45	59 24	59 24
am = 100 : 101	18	39 18—39 58	39 45	*
mc = 101 : 001	19	44 19—45 7	44 48	*
bc = 010 : 001	27	77 6—78 3	77 36	*
bk = 010 : 011	3	37 31—38 28	38 4	38 13
kc = 011 : 001	3	39 0—39 28	39 15	39 23
cq = 001 : $0\bar{1}1$	23	51 55—52 16	52 6	52 2
cl = 001 : $0\bar{1}2$	4	29 16—29 37	29 24	29 21
lq = $0\bar{1}2$: $0\bar{1}1$	4	22 26—22 54	22 41	22 41
qb = $0\bar{1}1$: $0\bar{1}0$	22	50 2—50 38	50 18	50 22
bm = 010 : 101	17	65 15—66 4	65 48	65 48
mr = 101 : $1\bar{1}1$	10	39 27—39 42	39 33	39 26
rb = $1\bar{1}1$: $0\bar{1}0$	10	74 26—74 57	74 38	74 46
ar = 100 : $1\bar{1}1$	11	56 13—57 8	56 54	56 53
rq = $1\bar{1}1$: $0\bar{1}1$	11	46 23—46 45	46 37	46 40
qa = $0\bar{1}1$: $\bar{1}00$	15	76 12—76 54	76 27	76 27
p′m = $1\bar{1}0$: 101	14	68 24—69 10	68 46	68 49
mk = 101 : 011	2	44 17—44 21	44 19	44 17
kp′ = 011 : $\bar{1}10$	2	66 39—67 3	66 51	66 54
p′r = $1\bar{1}0$: $1\bar{1}1$	11	42 14—42 48	42 29	42 30
rc = $1\bar{1}1$: 001	11	52 45—53 17	53 5	53 5
cp′ = 001 : $\bar{1}10$	19	84 11—84 41	84 25	84 25
p′q = $1\bar{1}0$: $0\bar{1}1$	13	70 7—70 31	70 20	70 28

There are cleavages parallel to the pinacoids *a* and *b* and a feeble one parallel to the basal plane *c*. In this respect the triclinic ethyl imide perfectly resembles the analogous methyl compound. In parallel polarised light, extinctions upon *a* and *b* are about 35° and 28° respectively. In convergent light, *b* shows an optic axis and rings towards the edge nearest to *a*.

The similarity between the triclinic methyl and the triclinic ethyl imides is graphically shown by the spherical projections of the two compounds, Figs. 10 and 18. A comparison between the measured angles common to both compounds is made in the following table:—

Angle.	Triclinio methyl.	Triclinio ethyl.	Angle.	Triclinic methyl.	Triclinio ethyl.
α	79° 52′	78° 48′	*am*	41° 2′	39° 45′
β	86 3	89 10	*mc*	41 5	44 48
γ	70 26	68 2			
			ar	55 36	56 54
ba	69 19	67 26	*rq*	43 23	46 37
ap	51 47	53 10	*qa*	81 1	76 27
pb	58 54	59 24			
			pm	67 56	68 46
bm	68 1	65 48			
mr	36 13	39 33	*pr*	43 44	42 29
rb	75 46	74 38	*rc*	49 14	53 5
			cp	87 2	84 25
bk	40 47	38 4			
kc	36 59	39 15	*pq*	69 29	70 20
cq	48 11	52 6			
qb	54 9	50 18			

The difference in the ratio of the axes caused by the introduction of an additional CH_2-group is shown in the following comparison:—

Triclinic methyl: $a : b : c = 0{\cdot}9059 : 1 : 0{\cdot}8695$.
Triclinic ethyl: $a : b : c = 0{\cdot}9120 : 1 : 0{\cdot}9524$.

From which it would appear that the ratio of $a : b$ is practically maintained, while the vertical c axis is slightly elongated.

Monoclinic Variety.

Melting point 129°.

The monoclinic crystals of ethyl triphenylpyrrholone are specially interesting as presenting a case of exceptionally large dispersion in crossed axial planes, similar to the case of brookite in the rhombic system.

They are brilliant, almost colourless crystals of which the faces are pretty evenly developed. The average diameter of the specimens examined was about 2 mm.

Axial angle: $\beta = 86° 54'$.
Ratio of axes: $a : b : c = 1{\cdot}6898 : 1 : 1{\cdot}9579$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $c = \{001\}oP$; $r = \{101\}-\bar{P}\infty$;
$r' = \{\bar{1}01\}+\bar{P}\infty$; $o = \{111\}-P$; $o' = \{\bar{1}11\}+P$;
$m = \{012\}\frac{1}{2}\bar{P}\infty$; $n = \{31\bar{1}\}+3\bar{P}3$; $s = \{11\bar{3}\}+\frac{1}{3}P$.

Fig. 19 shows the general form of the crystals, and Fig. 20 the spherical projection.

The principal faces which give shape to the crystals are the orthopinacoid *a*(100), the basal plane *c*(001), and the primary hemipyramids *o*(111) and *o*′($\bar{1}$11). The orthodome *r*(101) is generally present as a fairly broad truncation of the edge *ac*, and the clinodome *m* is also a fairly well developed form when present, but the remaining forms *r*′($\bar{1}$01), *n*(31$\bar{1}$), and *s*(11$\bar{3}$) are generally either small or absent.

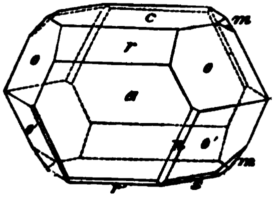


FIG. 19A.

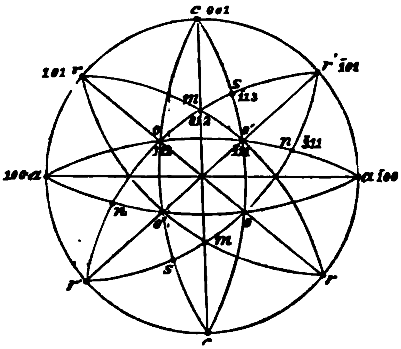


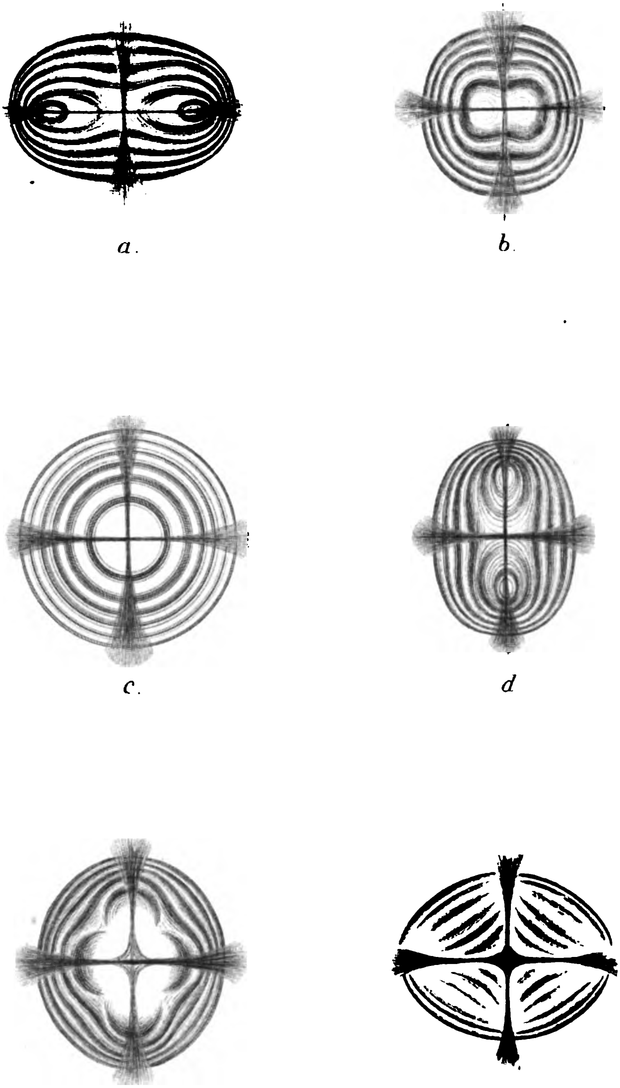
FIG. 20.

The following measurements were obtained :—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ar = 100 : 101	17	39° 4′—39° 50′	39° 28′	*
rc = 101 : 001	17	47 3—47 49	47 26	*
cr′ = 001 : $\bar{1}$01	—	—	—	50° 58′
r′*a* = $\bar{1}$01 : $\bar{1}$00	—	—	—	42 8
ca = 001 : $\bar{1}$00	20	92 47—93 26	93 6	93 6
ao = 100 : 111	40	60 5—61 38	61 6	61 5
oo′ = 111 : $\bar{1}$11	40	54 58—56 20	55 41	55 38
o′*n* = $\bar{1}$11 : $\bar{3}$11	5	30 28—30 41	30 35	30 36
na = $\bar{3}$11 : $\bar{1}$00	5	32 30—32 49	32 39	32 41
o′*a* = $\bar{1}$11 : $\bar{1}$00	40	62 48—63 51	63 18	63 17
ro = 101 : 11$\bar{1}$	37	50 30—51 40	51 13	*
oo = 111 : $\bar{1}$1$\bar{1}$	19	77 6—78 30	77 30	77 34
ro′ = 101 : 11$\bar{1}$	38	84 19—85 24	84 51	84 55
o′*m* = 11$\bar{1}$: 01$\bar{2}$	1	—	33 50	33 50
mr = 01$\bar{2}$: $\bar{1}$0$\bar{1}$	1	—	61 11	61 15
o′*r* = 11$\bar{1}$: $\bar{1}$0$\bar{1}$	38	94 23—95 41	95 8	95 5
co = 001 : 111	40	64 24—65 28	64 54	64 56
oo′ = 111 : 11$\bar{1}$	39	47 0—47 57	47 28	47 29
o′*s* = 11$\bar{1}$: 11$\bar{3}$	1	—	30 2	29 52
sc = 11$\bar{3}$: 00$\bar{1}$	—	—	—	37 43
o′*c* = 11$\bar{1}$: 00$\bar{1}$	39	67 4—68 2	67 38	67 35
r′*o*′ = 10$\bar{1}$: 11$\bar{1}$	4	52 28—52 44	52 37	52 42
o′*o*′ = 11$\bar{1}$: $\bar{1}$11	20	73 59—75 16	74 40	74 36
o′*o*′ = $\bar{1}$11 : $\bar{1}\bar{1}$1	20	104 47—106 2	105 20	105 24

Tutton. Journ. Chem. Soc. Aug. 1890.

Fig. 21



a. b. c. d e. f

There is an excellent cleavage parallel to the orthopinacoid *a*(100). A cleavage plate, or a thin crystal, laid upon the face *a* shows in convergent white light an exceptional and very beautiful interference figure. The figure is not symmetrical to the normal to *a*; it lies on that side of the field nearest the edge *ar*, and the first median line makes an angle of about 27° with the normal to *a* in the direction of *r*. On cutting a section parallel to the ortho-axis *b*, and making an angle of 27° with *a* and 12½° with *r*, the interference figure is seen symmetrical to the centre of the field. An idea of the appearance of this figure may be obtained from Fig. 21, *f*. Instead of the ordinary biaxial rings and lemniscates, the figure consists of a series of concave coloured curves falling in between the arms of the cross, and looping round four axes. This peculiar figure is due to the fact that the plane of the optic axis for red is at right angles to that for green light, the former being perpendicular and the latter parallel to the symmetry plane. On illuminating with lithium light, an ordinary biaxial figure is observed, as shown in Fig. 21, *a*. On changing to yellow sodium light, the figure is similar, but the axes are much nearer together, as seen at *b*, Fig. 21. On further changing to green thallium light, an ordinary biaxial figure is again obtained, as shown at *d* in Fig. 21, but the line joining the axes is now vertical, at right angles to that joining the axes for sodium and lithium light. For some particular wave-length in the greenish-yellow, the two axes coincide in the centre of the field, with production of an apparently uniaxial figure, as shown at *c* in Fig. 21. When a mixture of sodium and thallium light is employed, as when the thallium green is just dying out and the yellow flame of sodium is becoming stronger, the figure shown at Fig. 21, *e*, is obtained.

The following measurements of the angles of separation were made in air (2E) and in castor oil (2H*a*).

2E.

	By lithium light.		By sodium light.		By thallium light.
	32° 45′		17° 15′		21° 45′
	32 15		17 20		21 55
			17 30		
			17 20		
Mean..	32 30	Mean...	17 20	Mean..	21 50

			2Ha.		
	22° 10′		12° 10′		14° 55′
	22 20		12 30		14 50
	22 20		11 40		15 0
	22 5				
Mean..	22 15	Mean..	12 10	Mean..	14 55

For lithium and sodium light, the plane of the optic axes is perpendicular to the symmetry plane; the first median line lies in the symmetry plane and the two axes are symmetrically arranged on each side of it, separated in air 32° 30′ in case of lithium light. As the wave-length of the light diminishes, the axes close in upon the median line and approach the symmetry plane; for light of some particular wave-length between that of the D sodium line and that of the green thallium line, the two axes and the median line coincide, producing an apparently uniaxial figure, a cross and circular rings. As the wave-length continues to diminish, the axes again diverge, but remain in the symmetry plane, and attain a separation of 21° 50′ when thallium light is employed. Hence there is a total dispersion between these limits of 32° 30′ + 21° 50′ = 54° 20′ of the sign $\rho > v$.

The sign of double refraction, as determined by means of a quarter undulation plate, is negative.

The sections which show the interference figures best are somewhat thick, about 1 mm. The obtuse angle was too large to be visible through sections at right angles to second median line, even in oil.

Bromine-derivative of 1-*Ethyl*-3-*diphenyl*-5-*phenylpyrrholone*, $C_{24}H_{20}BrNO$.

Melting point 142°. Crystallised from carbon bisulphide.

The bromine-derivative of the ethyl compound forms large, yellow, transparent crystals, somewhat resembling those of the bromo-methyl imide. They crystallise in the same system, but are of different habit. They possess the peculiarity of rapidly becoming opaque; the edges become white, and lose their sharpness in a few hours, and the opacity then rapidly extends throughout the whole crystal. This appears to be probably due to the occurrence of a change to a more stable crystallographic form, possibly to one resembling that of the bromo-methyl compound.

System: monoclinic. Habit: prismatic $\beta = 80° 58'$.
Ratio of axes: $a : b : c = 1{\cdot}2102 : 1 : 0{\cdot}5602$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\bar{P}\infty$; $p = \{110\}\infty P$; $p' = \{210\}\infty\bar{P}2$; $r = \{101\} - \bar{P}\infty$; $s = \{\bar{1}01\} + \bar{P}\infty$; $o = \{111\} - P$ $n = \{\bar{1}11\} + P$; $t = \{121\} - 2\breve{P}2$.

The usual shape of the specimens examined is given in Fig. 22, and the spherical projection in Fig. 23.

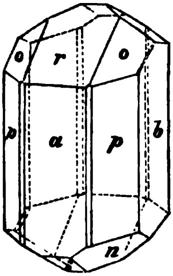


FIG. 22.

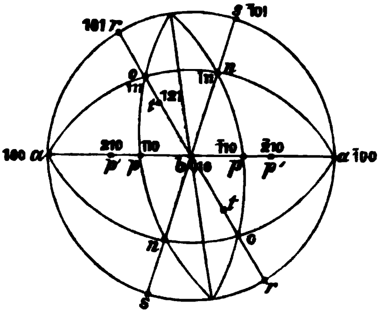


FIG. 23.

The crystals are typically monoclinic. The two pinacoids *a*(100) and *b*(010) and the prism (110) are about equally developed, and constitute a thick-set prism. The dome *r*(101) is the most important end face, its complement *s*($\bar{1}$01) being much smaller. Flanking *r* on each side are the faces of the primary hemi-pyramid *o*(111), not much smaller than *r* itself. The positive hemi-pyramid *n*($\bar{1}$11) is also fairly well developed, but *t*(121) is only present as a mere line.

The following measurements were obtained:—

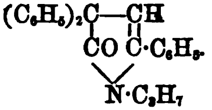
Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ap = 100 : 110	22	49° 1′—50° 46′	50° 5′	*
ap′ = 100 : 210	8	30 21 —31 30	30 55	30° 52′
p′p = 210 : 110	6	18 42 —19 53	19 11	19 13
pb = 110 : 010	20	38 54 —41 50	39 54	39 55
ar = 100 : 101	14	57 34 —58 30	57 53	*
rs = 101 : $\bar{1}$01	2	49 25 —49 36	49 30	49 24
sa = $\bar{1}$01 : $\bar{1}$00	2	72 20 —72 52	72 36	72 43
ao = 100 : 111	16	60 49 —61 57	61 18	61 18
on = 111 : $\bar{1}$11	13	43 28 —44 23	43 47	43 50
na = $\bar{1}$11 : $\bar{1}$00	14	74 24 —75 18	74 57	74 52
bo = 010 : 111	18	63 58 —65 6	64 37	*
to = 121 : 111	1	—	18 13	18 7
or = 111 : 101	17	24 21 —26 22	25 22	25 23
bn = 010 : $\bar{1}$11	18	61 22 —62 6	61 41	61 50
ns = $\bar{1}$11 : $\bar{1}$01	4	27 49 —28 21	28 11	28 10
op = 111 : 110	17	49 48 —50 58	50 22	50 26
pn = 110 : 11$\bar{1}$	15	57 43 —58 50	58 4	58 2
no = 11$\bar{1}$: $\bar{1}\bar{1}\bar{1}$	11	70 49 —72 4	71 31	71 32

There is a cleavage parallel to the symmetry plane *b*(010).

Owing to the rapidity with which the crystals become opaque, the optical properties could not be very completely studied. Sections became completely opaque within 5 to 10 minutes of grinding.

The symmetry plane is also the plane of the optic axes. Both axes are seen through *a* (100) in convergent light. The median line emerges at an angle of about 5—10° from the normal to the plate towards the edge *ar*. The axis nearest the centre of the field makes an angle of about 42° with the normal. A section was cut perpendicular to the median line, but was too opaque for accurate measurement of the angle between the axes. There was just time as the opacity was developing to see that the axes and rings were then symmetrical to the centre of the field.

Propyl Triphenylpyrrholone,



$$\begin{array}{l}(C_6H_5)_2C{-}CH\\ \quad CO\quad C{\cdot}C_6H_5.\\ \qquad N{\cdot}C_3H_7\end{array}$$

Two varieties of the propyl imide have been obtained, a monoclinic variety, apparently completely isomorphous with the monoclinic ethyl compound, and a rhombic variety. As propylamine does not react as readily as ethylamine and methylamine, it was found necessary to conduct the preparation from alcoholic dibenzoylcinnamene at 100° in a sealed tube.

Monoclinic Variety.—Melting point 95—98°. The variety was only obtained in one experiment, but the preparation was a very fine one, consisting of exceptionally large, colourless crystals of great brilliancy, averaging 5—10 mm. by 3—7 and 3—5 mm. in size. They were usually slightly tabular, upon various planes, according to their position in respect to the walls of the vessel in which crystallisation occurred. Their external resemblance to the monoclinic crystals of the ethyl compound is most striking, as will be seen on comparing Fig. 19 with Fig. 24. All the planes of any importance exhibited by the ethyl imide are represented also upon the crystals of the propyl compound.

Axial angle: $\beta = 86° \, 17'$.
Ratio of axes: $a : b : c = 1{\cdot}8060 : 1 : 1{\cdot}8821$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\grave{P}\infty$; $c = \{001\}oP$;
$r = \{101\}-\bar{P}\infty$; $r' = \{\bar{1}01\}+\bar{P}\infty$; $o = \{111\}-P$; $o' = \{\bar{1}11\}+P$;
$q = \{011\}\grave{P}\infty$; $m = \{012\}\tfrac{1}{2}\grave{P}\infty$; $p = \{210\}\infty\bar{P}2$; $n = \{31\bar{1}\}+3\bar{P}3$;
$t = \{113\}-\tfrac{1}{3}P$.

The description of the relative development of the various forms exhibited by the monoclinic ethyl compound is perfectly applicable to the case of the propyl imide. The clinopinacoid *b*(010) was noticed upon one or two crystals of the latter compound, as was also the clinodome *q*(011). Instead of the hemi-pyramid *s*(11$\bar{3}$) of the ethyl compound, the complementary form *t*(113) was found upon one crystal of the propyl imide.

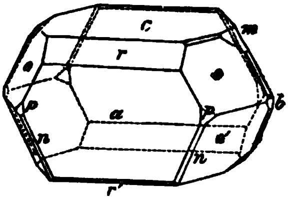


FIG. 24.

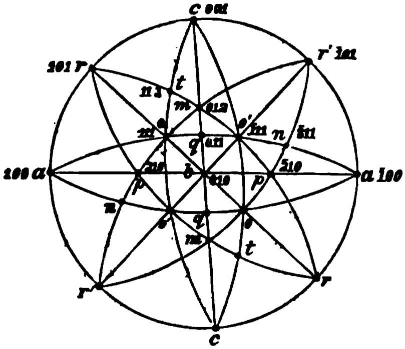


FIG. 25.

The following table gives the results of the angular measurements:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ar = 100 : 101	15	41° 35′— 42° 22′	42° 2′	*
rc = 101 : 001	15	43 52 — 44 34	44 15	*
cr′ = 001 : $\bar{1}$01	1	—	48 19	48° 7′
r′a = $\bar{1}$01 : $\bar{1}$00	1	—	45 33	45 36
ca = 001 : $\bar{1}$00	17	93 2 — 94 9	93 41	93 43
ao = 100 : 111	32	61 58 — 63 5	62 30	62 30
oq = 111 : 011	1	—	25 56	25 44
qo′ = 011 : $\bar{1}$11	1	—	26 23	26 24
oo′ = 111 : $\bar{1}$11	32	51 23 — 52 48	52 16	52 11
o′n = $\bar{1}$11 : $\bar{3}$11	2	29 58 — 30 44	30 21	30 27
na = $\bar{3}$11 : $\bar{1}$00	2	34 35 — 35 4	34 49	34 52
o′a = $\bar{1}$11 : $\bar{1}$00	36	64 51 — 65 54	65 15	65 19
ro = 101 : 111	32	51 2 — 51 58	51 34	*
ob = 111 : 010	2	38 36 — 38 37	38 36	38 26
oo = 111 : $\bar{1}$1$\bar{1}$	14	76 32 — 77 18	76 53	76 52
rp = 101 : 210	1	—	56 23	56 26
po′ = 210 : 11$\bar{1}$	1	—	32 10	32 9
ro′ = 101 : 11$\bar{1}$	26	88 13 — 89 14	88 33	88 35
o′m = 11$\bar{1}$: 01$\bar{2}$	3	32 36 — 32 57	32 47	32 51
mt = 01$\bar{2}$: $\bar{1}$1$\bar{3}$	1	—	19 57	19 54
tr = $\bar{1}$1$\bar{3}$: $\bar{1}$0$\bar{1}$	1	—	38 32	38 40
o′r = 11$\bar{1}$: $\bar{1}$0$\bar{1}$	26	91 3 — 91 48	91 28	91 25
om = 001 : 012	1	—	43 5	43 16
mq = 012 : 011	1	—	18 43	18 45

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ct = 001 : 113	1	—	34 58	34 54
to = 113 : 111	1	—	28 40	28 40
co = 001 : 111	33	63 2 — 64 13	63 37	63 34
oo′ = 111 : 11$\bar{1}$	33	49 24 — 50 21	49 55	49 55
o′c = 11$\bar{1}$: 00$\bar{1}$	36	65 47 — 67 5	66 27	66 31
r′o′ = 10$\bar{1}$: 11$\bar{1}$	2	53 6 — 53 32	53 19	53 22
o′o′ = 11$\bar{1}$: $\bar{1}$11	16	72 30 — 73 41	73 19	73 16
o′o′ = $\bar{1}$11 : $\bar{1}\bar{1}$1	14	106 9 — 107 18	106 38	106 44

There is a very perfect cleavage parallel to the orthopinacoid *a*(100), as in case of the ethyl-derivative.

The plane of the optic axes is perpendicular to the symmetry plane, and the first median line makes an angle of about 10° with the normal to *a*(100). This angle was determined by observing the direction of extinction upon a section cut parallel to the symmetry plane. This section showed in convergent light the two axes and rings separated at their obtuse angle, which was too large for measurement even in oil, the axes being only just seen when the section was tilted almost vertically on each side. A crystal tabular upon the orthopinacoid *a*(100), or a cleavage plate, shows both axes at their acute angle, not quite in centre of field, the median line being, of course, 10° from centre. A section cut, as exactly as possible, perpendicular to the first median line shows both axes symmetrical to the centre of the field. It is evident from the interference figure that the dispersion is very strong, for on rotating the section the hyperbolic brushes are seen to be extremely highly coloured, appearing as spectrum curves, resembling the rainbow, instead of black ones. It is not so great, however, as to lead to a crossing of the axial planes as in case of the ethyl analogue.

The following measurements of the acute angle between the optic axes in air and in castor oil were made:—

	By lithium light.	By sodium light.	By thallium light.
In air 2E.	79° 30′	76° 25′	68° 35′
In oil 2Ha.	50° 40′	49° 10′	43° 20′

There is, therefore, a dispersion between these limits of about 11°, when the measurements are made in air, of the order $\rho > v$.

The sign of the double refraction, as in the crystals of the ethyl compound, is negative.

A comparison between the measured angles common to the monoclinic ethyl and propyl imides is made in the following table:—

Angle.	Monoclinic ethyl.	Monoclinic propyl.	Angle.	Monoclinic ethyl.	Monoclinic propyl.
β	86° 54′	86° 17′	*ro*	51° 13′	51° 34′
			oo	77 30	76 53
ar	39 28	42 2			
rc	47 26	44 15	*ro′*	84 51	88 33
cr′	50 58	48 19	*o′m*	33 50	32 47
r′a	42 8	45 33	*mr*	61 11	58 29
ca	93 6	93 41	*o′r*	95 8	91 28
ao	61 6	62 30	*co*	64 54	63 37
oo′	55 41	52 16	*oo′*	47 28	49 55
o′n	30 35	30 21	*o′c*	67 38	66 27
na	32 39	34 49			
o′a	63 13	65 15	*r′o′*	52 37	53 19
			o′o′	74 40	73 19

This similarity in the angles is at once apparent upon comparing the spherical projection of the monoclinic ethyl compound, Fig. 20, with that of the propyl analogue, Fig. 25.

Rhombic Variety.

Melting point 104—105°.

This was the form in which the propyl compound was usually deposited on allowing the contents of the sealed tube to cool and evaporate.

The crystals take the form of colourless prisms, 3—5 mm. long, and 2—3 × 1—2 mm. in section.

Ratio of axes: $a : b : c = 0{\cdot}6494 : 1 : 0{\cdot}7646$.

Forms observed: $b = \{010\}\infty\breve{P}\infty$; $p = \{110\}\infty P$; $p' = \{210\}\infty\bar{P}2$;
$p'' = \{170\}\infty\breve{P}7$; $q = \{011\}\breve{P}\infty$; $n = \{012\}\tfrac{1}{2}\breve{P}\infty$;
$m = \{032\}\tfrac{3}{2}\breve{P}\infty$; $r = \{101\}\bar{P}\infty$.

Figs. 26 and 27 show the usual appearance of the crystals and their spherical projection.

The forms which give shape to the crystals are the prism *p*(110) and the brachydomes *q*(011) and *n*(012), which are invariably present; *n* is generally somewhat smaller than *q*. The brachypinacoid *b*(010) faces in the specimens examined were generally narrow; the prisms *p′*(210) and *p″*(170) were only found occasionally. The macrodome *r*(101) is generally a well-formed face, but not so fully developed as *q*(011).

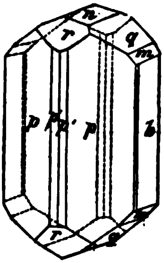


FIG. 26.

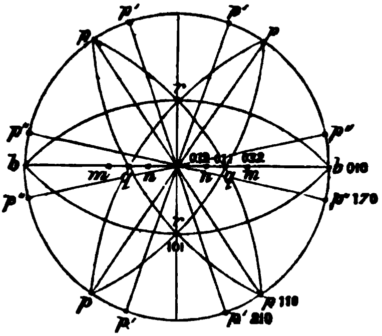


FIG. 27.

Following is a table of the angles measured:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
bp = 010 : 110	40	56° 20′—57° 48′	57° 3′	57° 0′
bp″ = 010 : 170	2	12 4—12 59	12 31	12 24
pp′ = 110 : 210	4	14 36—15 36	14 57	15 1
bq = 010 : 011	29	52 22—53 12	52 36	*
bm = 010 : 032	1	—	41 10	41 5
qn = 011 : 012	16	16 8—16 39	16 24	16 29
rr = 101 : $\bar{1}01$	4	99 4—99 34	99 16	99 18
rr = 101 : $10\bar{1}$	5	80 5—81 15	80 42	80 42
pr = 110 : 101	41	49 58—50 47	50 21	50 16
pq = 110 : 011	46	70 16—71 19	70 41	*

There is a good cleavage parallel to the brachydome *q*(011).

Several twins were found twinned upon the prism face *p*(110).

The plane of the optic axes is the macropinacoid *a*(100). The vertical axis *c* is the first median line.

A section cut perpendicular to the vertical axis *c* and parallel to the possible basal plane (001), when viewed in convergent light in air, just shows the two axes and their rings at the extreme right and left hand edges of the field. They are much better seen in oil. A second section parallel to the brachypinacoid *b*(010) was also cut, and also showed in oil the two axes separated at their obtuse angle.

The following measurements of the apparent acute and obtuse angles for sodium light were obtained:—

2E. Acute angle in air.	2H*a*. Acute angle in oil.	2H*o*. Obtuse angle in oil.
135° 10′	77° 45′	132° 30′
135 30	77 40	132 50
136 10	77 45	
135 20		
Mean.. 135 30	Mean.. 77 45	Mean.. 132 40

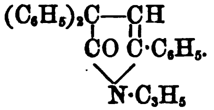
The true angle $2Va$ between the optic axes, calculated by means of the formula $\tan Va = \frac{\sin Ha}{\sin Ho}$, is 68° 50′.

The mean refractive index of the crystals, β, calculated from the apparent angle of the optic axes in air and the true angle by means of the formula $\beta = \frac{\sin E}{\sin Va}$, is found to be 1·6377.

The dispersion is very small, of the sign $\rho > v$, the hyperbolic brushes being bordered with blue outside and red inside.

The sign of double refraction is positive.

Allyl Triphenylpyrrholone,



$$(C_6H_5)_2C{-}CH \quad CO \; C{\cdot}C_6H_5. \quad N{\cdot}C_3H_5$$

Melting point 110—112°. Like the propyl compound, the allyl-derivative was prepared by heating alcoholic allylamine and dibenzoylcinnamene together in a sealed tube at 100°.

The allyl compound forms colourless, evenly-developed crystals of 1—3 mm. diameter.

System: monoclinic. $\beta = 88°\ 53'$; hence the crystals simulate rhombic symmetry very closely. Their truly monoclinic character is proved by their optical characters as well as by the slight deviations of the angles from those required for rhombic symmetry.

Ratio of axes: $a : b : c = 1{\cdot}6654 : 1 : 1{\cdot}8441$.

Forms observed: $a = \{100\}\infty\bar{P}\infty$; $b = \{010\}\infty\breve{P}\infty$; $c = \{001\}oP$; $p = \{110\}\infty P$; $p' = \{210\}\infty\bar{P}2$; $r = \{101\}-\bar{P}\infty$; $s = \{102\}-\frac{1}{2}\bar{P}\infty$; $r' = \{\bar{1}01\}+\bar{P}\infty$; $s' = \{\bar{1}02\}+\frac{1}{2}\bar{P}\infty$; $q = \{011\}\breve{P}\infty$; $m = \{012\}\frac{1}{2}\breve{P}\infty$; $n = \{112\}-\frac{1}{2}P$; $n' = \{\bar{1}12\}+\frac{1}{2}P$; $t = \{\bar{1}22\}+\breve{P}2$.

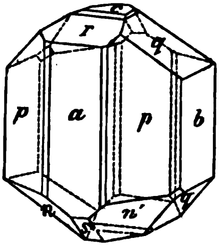


FIG. 28.

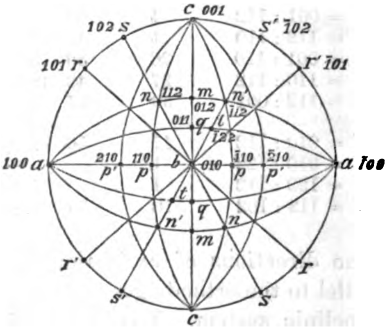


FIG. 29.

A typical crystal is represented in Fig. 28, and its spherical projection in Fig. 29.

The best developed forms are the prism *p*(110), the two pinacoids *a*(100) and *b*(010), the basal plane *c*(001), the clinodome *q*(011), and the hemi-prism *n*′($\bar{1}$12). The remaining faces are small, and not always present. The planes *a*, *b*, *c*, *p*′, *r*, *r*′, *q*, and *m* correspond to those marked with the same letters upon the monoclinic variety of the propyl compound. The angles between these faces are very similar in the two compounds, and a comparison table is given at the end of the present description.

The angles measured upon the allyl imide are as follows:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ap = 100 : 110	23	58° 49′—59° 34′	59° 2′	*
ap′ = 100 : 210	4	39 30 —40 2	39 52	39° 48′
p′*p* = 210 : 110	5	18 54 —20 20	19 20	19 14
pb = 110 : 010	15	30 37 —31 5	30 54	30 58
ar = 100 : 101	18	41 3 —41 57	41 33	41 35
rs = 101 : 102	5	17 59 —19 46	18 41	18 36
sc = 102 : 001	6	27 40 —29 38	28 46	28 42
cs′ = 001 ; $\bar{1}$02	2	29 5 —29 19	29 12	29 15
s′*r*′ = $\bar{1}$02 : $\bar{1}$01	2	18 45 —19 58	19 21	19 18
r′*a* = $\bar{1}$01 : $\bar{1}$00	2	42 31 —42 40	42 35	42 34
bq = 010 : 011	7	28 3 —28 52	28 28	28 27
qm = 011 : 012	23	18 17 —19 8	18 47	18 51
mc = 012 : 001	23	42 16 —43 14	42 40	42 42
an = 100 : 112	4	67 7 —67 15	67 12	67 10
nm = 112 : 012	3	21 47 —22 7	21 58	22 2
am = 100 : 012	21	88 32 —89 46	89 17	89 12
mn = 012 : $\bar{1}$12	21	21 52 —22 29	22 10	22 15
na = $\bar{1}$12 : $\bar{1}$00	36	68 17 —69 5	68 33	*
aq = 100 : 011	32	89 4 —89 56	89 33	89 28
qa = 011 : $\bar{1}$00	32	90 5 —91 24	90 29	90 32
cn = 001 : 112	4	46 39 —46 51	46 44	46 48
np = 112 : 110	4	42 33 —42 51	42 41	42 38
cp = 001 : 110	26	89 5 —89 51	89 27	89 26
pn′ = 110 : 11$\bar{2}$	27	42 48 —43 19	43 9	*
n′*c* = 11$\bar{2}$: 00$\bar{1}$	39	47 3 —47 48	47 23	47 25
bn′ = 010 : $\bar{1}$12	17	50 14 —51 29	50 53	50 51
bt = 010 : $\bar{1}$22	1	—	31 22	31 33
tn′ = $\bar{1}$22 : $\bar{1}$12	1	—	19 16	19 18
n′*s*′ = $\bar{1}$12 : $\bar{1}$02	18	39 0 —39 17	39 6	39 9

The directions of extinction upon faces in the zone [*a*, *r*, *c*] are parallel to the orthodiagonal, in accordance with the symmetry of the monoclinic system. The plane of the optic axes is the symmetry plane. Through the basal plane *c*(001), in convergent light, a brush is seen of which the axis lies just outside the field in the direction of $s'(\bar{1}02)$.

From the above description, it will be evident that the allyl compound bears many resemblances to the monoclinic varieties of the ethyl and propyl compounds. The morphotropical relationship, as was to be expected, is not so close as between the two latter compounds themselves. Nevertheless, the similarity of the angles in several of the zones is very striking, and is shown in the following tabular comparison :—

Angle.	Propyl compound.	Allyl compound.
ar	42° 2′	41° 33′
rc	44 15	47 27
cr′	48 19	48 33
r′a	45 33	42 35
bq	28 12	28 28
qm	18 43	18 47
mc	43 5	42 40
ap	41 52	39 52
ro	51 34	50 45 calculated.

Ratio of axes of propyl imide .... 1·8060 : 1 : 1·8821.
,, allyl ,, ... 1·6654 : 1 : 1·8441.

It is somewhat interesting to note that the substitution of the unsaturated allyl for the saturated propyl radicle, which is practically the removal of two atoms of hydrogen from the propyl imide, is accompanied by a diminution in the length of the *a* axis as compared with that of the *b* axis, while the ratio of the *c* to the *b* axis remains almost the same.

The Compound $C_{21}H_{16}O$, *obtained by the Distillation of αβ-Dibenzoylcinnamene.*

Melting point 92—93°. Crystallised from ether.

This substance forms splendid, yellowish-green crystals of great brilliancy, varying in size up to 4 mm. diameter. Many of the crystals gave reflections as perfect as those from a metallic mirror.

System: monoclinic. Habit: inclined to be tabular upon the basal plane.
Axial angle: $\beta = 67° 47'$.
Ratio of axes: $a : b : c = 1·9640 : 1 : 1·0331$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $c = \{001\}oP$; $p = \{110\}\infty P$, $o = \{\bar{1}11\} + P$; $r = \{\bar{2}01\} + 2\bar{P}\infty$.

These crystals are typically monoclinic in appearance, as may be seen from an inspection of Fig. 30. The prism zone, including the prism $p(110)$ and the orthopinacoid $a(100)$, is always well developed, but the faces are not so long as to render the substance prismatic in habit. The basal plane $c(001)$ is generally the predominating end face, and frequently the crystals are tabular upon it, but always retaining a fair amount of thickness. The orthodome $r(\bar{2}01)$ is generally small compared with c, but occasionally crystals are found exhibiting both equally developed. The faces of the hemi-pyramid $o(\bar{1}11)$ generally occurred as mere lines truncating the edges cp, $(001) : (\bar{1}10)$, but were sometimes found more largely developed.

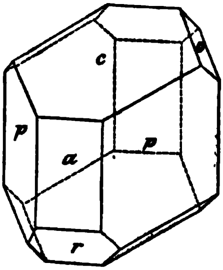


FIG. 30.

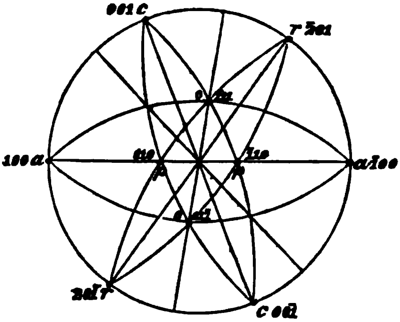


FIG. 31.

The following measurements were obtained:—

Angle measured.	No. of measurements.	Limits.	Mean observed.	Calculated.
ap = 100 : 110	47	60° 9′ — 61° 48′	61° 11′	*
pp = 110 : $\bar{1}$10	24	57 10 — 58 44	57 38	57° 38′
ac = 100 : 001	24	67 18 — 68 6	67 44	67 47
cr = 001 : $\bar{2}$01	21	57 46 — 58 39	58 19	58 14
ra = $\bar{2}$01 : $\bar{1}$00	21	53 36 — 54 19	53 57	53 59
cp = 001 : 110	88	79 5 — 79 59	79 30	*
po = 110 : 11$\bar{1}$	28	46 59 — 47 31	47 13	47 16
oc = 11$\bar{1}$: 00$\bar{1}$	28	52 45 — 53 38	53 17	53 14
ro = $\bar{2}$01 : $\bar{1}$11	25	50 46 — 51 51	51 22	51 22
op = $\bar{1}$11 : 110	25	54 30 — 55 43	55 6	55 6
pr = 110 : 20$\bar{1}$	36	73 1 — 73 58	73 32	*
ao = 100 : $\bar{1}$11	23	95 59 — 96 54	96 24	96 20
oa = $\bar{1}$11 : $\bar{1}$00	20	83 21 — 83 50	83 36	83 40
oo = 11$\bar{1}$: $\bar{1}$11	8	88 40 — 89 1	88 51	88 56
oo = $\bar{1}$11 : $\bar{1}\bar{1}$1	8	90 59 — 91 17	91 9	91 4

There is a cleavage parallel to the orthopinacoid *a*(100), and a much less perfect one parallel to the symmetry plane.

The optic axial plane is the symmetry plane. In convergent light, on looking through *c*, an optic axis and rings are seen lying in the trace of the symmetry plane. The axis appears to emerge at an angle of about 25° with the normal to *c*, in the direction of the orthopinacoid *a*.

Oxylepidenic Acid.

Melting point 174—175°. Crystallised from alcohol.

Two distinct preparations were examined, one consisting of ordinary oxylepidenic acid and the other corresponding to an iso-oxylepidenic acid described by Zinin. Drs. Japp and Klingemann had obtained chemical evidence that the two were identical and not isomeric, as supposed by Zinin, and it was an interesting question as to whether the crystalline forms also were identical or not.

The preparation marked "oxylepidenic acid" consisted of minute, yellow prisms, while that labelled "isoxylepidenic acid ?" consisted of similar prisms of a greyish-green colour.

The two preparations are certainly cystallographically identical. That they are one and the same substance may be seen at once on consulting the comparative table of angles given.

Oxylepidenic acid is peculiar in crystallographical character. From the measurements, which are only approximate, owing to distortion and striation, it might be regarded as either hemihedral-tetragonal or rhombic. As shown in the drawing (Fig. 32), the crystals take the form of a flattened prism of which the face marked *c* is best developed. The narrower face *a* makes an angle so close to 90° with *c*, that the measured differences fall within the limits of error.

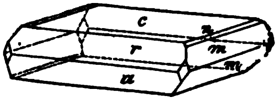


FIG. 32.

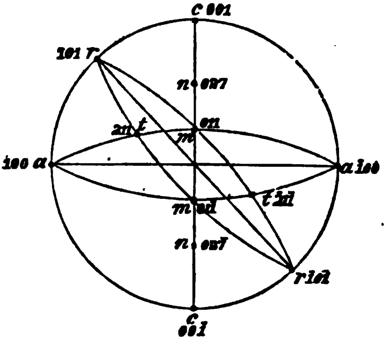


FIG. 33.

Further, the face *r* is situated almost exactly at 45° from *a* and *c*. As no corresponding face on the other side of *c* is present, the crystals cannot be holohedral, if tetragonal. The remaining faces may be accounted for either by the supposition of tetragonal or rhombic symmetry.

The optical properties, however, show that the crystals are certainly biaxial, and that they really belong to the monolinic system. On looking through the face *c*, which is considered as the basal plane (001), an optic axis with its brush and rings is seen in the trace of the symmetry plane, and on that side of the centre furthest from the edge *r*. That is, when the plate is arranged so that in parallel light extinction occurs, the crystallographical axial edges being parallel to the crossed Nicols, and when the converging system of lenses are then placed in position, the brush forms a straight line, which lies in a diameter of the field in the trace of the symmetry plane. The plane of the optic axes is, therefore, the symmetry plane.

System: monoclinic. $\beta = 89° 51'$. Habit: prismatic.
Ratio of axes: $a : b : c = 2{\cdot}1257 : 1 : 2{\cdot}1425$.
Forms observed: $a = \{100\}\infty\bar{P}\infty$; $c = \{001\}oP$; $r = \{101\} - \bar{P}\infty$;
$m = \{011\}\grave{P}\infty$; $n = \{027\}\frac{2}{7}\grave{P}\infty$; $t = \{211\} - 2\bar{P}2$.

Of the end forms *m*(011) is the most important; frequently it is the only form present besides *a*, *r*, and *c*. The hemi-pyramid *t*(211) occurs as small corner faces, and *n*(027) as a line just blunting the edge *cm*.

The following table shows the values of the various angles measured, both upon the preparation marked "oxylepidenic acid" and that labelled "isoxylepidenic acid ?"

Angle measured.	Measured on isoxylepidenic ? acid.	No. of measurements.	Measured on oxylepidenic acid.	No. of measurements.	Calculated.
ar = 100 : 101	44° 42′	6	44° 40′	2	*
rc = 101 : 001	45 9	6	45 10	3	*
ca = 001 : $\bar{1}00$	90 7	6	90 10	4	90° 9′
cn = 001 : 027	31 25	1	—	—	31 27
nm = 027 : 011	33 46	1	—	—	33 31
cm = 001 : 011	64 58	5	65 9	5	*
mm = 011 : $01\bar{1}$	49 37	2	49 43	2	50 4
at = 100 : 211	49 31	5	—	—	49 29
tm = 211 : 011	40 6	5	—	—	40 27
ma = 011 : $\bar{1}00$	89 50	5	—	—	90 4
rt = 101 : 211	46 33	4	—	—	46 31
tm = 211 : $01\bar{1}$	60 23	4	—	—	60 51
mr = $01\bar{1}$: $\bar{1}0\bar{1}$	72 27	4	—	—	72 38

Owing to the imperfect formation of many of the faces, the above values cannot be considered as nearer the truth than about 10′. The limits of the actual observations average about 20′ on each side of the mean values given. But the results are quite conclusive as to the identity of the so-called "isoxylepidenic acid" with ordinary oxylepidenic acid. The disposition of the faces was in all cases similar, *c* being invariably the best developed face, and the optical properties of the two preparations were identical. In the case of the preparation marked oxylepidenic acid, the crystals rarely showed the faces *n* and *t*, but this, which often happens with different preparations of the same substance, was the only point of difference observed.

L.—*Action of Carbon Monoxide on Nickel.*

By LUDWIG MOND, DR. CARL LANGER, and DR. FRIEDRICH QUINCKE.

WHEN carbon monoxide is passed over finely-divided metallic nickel at a temperature between 350° and 450°, carbon dioxide is formed, and a black, amorphous powder is obtained consisting of nickel and carbon. The composition of this powder varies very widely with the temperature employed, and still more according to the time the operation has been carried on. A small quantity of nickel can decompose a very large amount of carbon monoxide. At the commencement, a fast current of carbon monoxide is completely changed into carbon dioxide by a comparatively small quantity of nickel. By-and-by, the change becomes less complete, but the gas may be passed for several weeks before carbon dioxide ceases to be formed.

We have in this way obtained a product containing as much as 85 per cent. carbon and 15 per cent. nickel. By treating this product with acids, a certain portion of the nickel goes into solution; but we have not been able to extract the nickel completely, the minimum quantity remaining after treatment with concentrated sulphuric acid being 5·59 per cent.; by treatment with dilute hydrochloric acid, 9·30 per cent.*

In order to determine the nickel in this substance, we have heated it with concentrated sulphuric acid to about 200°, and then added nitrate of potash in small portions to oxidise the carbon. This was the only way by which we could obtain a perfectly clear solution, and from this the nickel was precipitated in the usual way. The combustion of the substance with copper oxide or lead chromate in a current of oxygen did not give satisfactory results.

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* Gautier and Hallopeau (*Compt. rend.*, **108**, 1889, 1111) obtained a similar product containing 20·05 per cent. of nickel and 79·95 per cent. carbon, by acting with bisulphide of carbon on metallic nickel.

The carbon contained in this substance is very readily attacked by steam; at the comparatively low temperature of 350°, hydrogen and carbon dioxide are obtained without a trace of carbon monoxide.

When we allowed this substance to cool while a current of carbon monoxide was being passed over it, we noticed that the flame of a Bunsen burner into which the escaping gas was introduced became highly luminous, and when we heated the tube through which the gas passed, we obtained a metallic mirror which proved to be nickel mixed with a small quantity of carbon.

After further investigating this subject, we found that the gas contains a compound of nickel and carbon monoxide, which we propose to call nickel-carbon-oxide.

When a finely-divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400° is allowed to cool in a slow current of carbon monoxide, this gas is very readily absorbed as soon as the temperature has descended to about 100°, and if the current of carbon monoxide is continued, or if this gas is replaced by a current of an inert gas (such as carbon dioxide, nitrogen, hydrogen, or even air) a mixture of gases is obtained which contains upwards of 30 per cent. of nickel-carbon-oxide. After a time (with a moderate current of gas, about an hour), the quantity of this compound given off becomes less and gradually diminishes till it practically ceases altogether. The property of the nickel to form this compound is restored by heating it again to about 400°, and cooling it down; and, for a time, it yields the compound more abundantly after repeated use. When these mixtures of gases are heated above 150°, their volume increases and nickel separates, which, according to the temperature, is more or less contaminated with carbon resulting from the action of the nickel upon the carbon monoxide generated.

After ascertaining that at a temperature of 180° nickel quite free from carbon is deposited, we have analysed these mixtures of gases, after absorbing the excess of carbon monoxide by cuprous chloride, by passing them repeatedly through a capillary tube inserted in aniline vapour until the volume became constant, weighing the nickel deposited in the tube, and ascertaining the volume of carbon monoxide formed by this decomposition. This volume was found to be in the proportion of 4 to 3 to the volume by which the original gas had been increased, thus proving that one volume of our compound gives 4 volumes of carbon monoxide. We give the result of several analyses, which lead to the formula $Ni(CO)_4$.

Gas volume.	After decomposition.	Expansion.	CO formed.	N.	Deposited Ni.
1. 28·3 c.c.	59·8	31·5	41·8	18·0	0·0260 gram
2. 48·5 c.c.	96·0	47·5	63·3	32·7	0·0438 „

For 100 c.c. of the nickel-carbon-oxide vapour (gas volume—nitrogen) this comes to—

(1.) 405·9 c.c. CO and 0·2527 gram Ni.
(2.) 400·5 c.c. CO and 0·2772 gram Ni.

The formula $Ni(CO)_4$ requires 400 c.c. CO and 0·2615 gram Ni.

The vapour of nickel-carbon-oxide when mixed with other gases is not acted upon by alkalis or acids; but it reduces a solution of copper chloride in ammonia, which becomes first decolorised and subsequently copper is precipitated from it. It also throws down silver from ammoniacal solutions of silver chloride. Chlorine decomposes it with formation of nickel chloride and carbon oxychloride. Bromine has a similar action. An electric spark decomposes it slowly into nickel and carbon monoxide. The presence of this vapour in other gases is very readily shown by the luminosity of the Bunsen flame into which it is introduced; very small quantities still show red luminous streaks.

If a mixture of gases containing the vapour of nickel-carbon-oxide is passed through a tube placed in a refrigerating mixture of salt and ice, the nickel-carbon-oxide is condensed to a colourless, mobile liquid of very high refractive power.

To obtain some quantity of this liquid, a combustion tube is filled with nickel oxide, the oxide reduced at about 400° by hydrogen, cooled down to about 30°, and pure and dry carbon monoxide is then passed through this tube without further heating it; the gas issuing from the tube is passed through a Y-tube surrounded by a freezing mixture of salt and ice. The lower end of this tube projects through the vessel containing the freezing mixture, and is connected to a small flask in which the condensed liquid accumulates. The gas, which on leaving the Y-tube still contains about 5 vols. per cent. of nickel-carbon-oxide, is collected, dried, and passed repeatedly over the nickel. When no more liquid condenses, the tube containing the nickel is heated up to about 400° in a slow current of pure hydrogen, cooled down again, and the operation recommenced. In this way we obtained from 10 to 15 grams of liquid in each operation.

The boiling point of this liquid, we found to be 43° at 751 mm.

pressure. Its sp. gr. is 1·3185 at 17°; at − 25° it solidifies, forming needle-shaped crystals.

The liquid is soluble in alcohol, but more readily soluble in benzene and chloroform. It is not acted upon by dilute acids and alkalis or by concentrated hydrochloric acid. Concentrated nitric acid and aqua regia oxidise it readily.

We have determined the nickel in this liquid by vaporising it in a current of hydrogen, and passing the vapour repeatedly through a U-tube heated in aniline vapour, and weighing the nickel deposited; and the carbon, by passing the vapour in a current of air over copper oxide, and weighing the carbon dioxide formed. We have thus obtained the following results:—

I. 0·0917 gram substance gave 0·0306 gram nickel = 33·35 per cent.

II. 0·0950 gram substance gave 0·0316 gram nickel = 33·37 per cent.

III. 0·2410 gram substance gave 0·2556 gram CO_2 = 66·60 per cent. CO.

IV. 0·2672 gram substance gave 0·2736 gram CO_2 = 65·99 per cent. CO.

The formula $Ni(CO)_4$ requires 34·34 per cent. nickel and 65·66 per cent. CO. The difference between the calculated amounts and the amounts found is probably due to carbon monoxide dissolved in the liquid.

The vapour density of the liquid determined by Victor Meyer's method at 50° has given the following figures:—

0·1052 gram substance displaced 14·4 c.c. air measured moist at 16° and 768 mm. pressure.

From this it follows that the density is 6·01. The formula $Ni(CO)_4$ requires 5·9. At a temperature of 60°, the vapour of the liquid explodes violently. This is the first determination of the vapour density of a compound of nickel, and shows the atomic volume of nickel to be near 58.

We have at present no suggestion to offer as to the constitution of this remarkable compound, but it is our intention to fully investigate this problem, and more particularly to study its action upon organic bodies.

Numerous experiments made to obtain similar compounds of carbon monoxide with other metals, notably with cobalt, iron, copper, and platinum, have only led to negative results, although they were carried out at temperatures from 15° to 750°. In experimenting with specially purified metallic cobalt, we obtained in the beginning a small coloration of the Bunsen flame, which completely disappeared after some time. In using commercial cobalt, we obtained a gas which yielded metallic mirrors. These, however, consisted of pure nickel, and did not show any of the reactions of cobalt. It seems thus possible to purify cobalt entirely from nickel by treating it with carbon monoxide. The metallic mirrors which we obtained from the nickel-carbon-oxide gave remarkably pure nickel reactions, and did not show a trace of any of the reactions of cobalt. The metal obtained from these mirrors by solution in acid, precipitation with ammonia, and reduction with hydrogen is a grey, metallic powder, the specific gravity of which we found to be 8·2834 at 15·4° and 8·2928 at 15·1°. The very finely divided metal is easily soluble in acids.

We had obtained a small quantity of this pure metal from a considerable quantity of nickel which had been under treatment. It appeared to us worth while to approximately determine the atomic weight of this pure metal, as this might throw some light upon the elementary nature of nickel and its real atomic weight, which have recently been called in question by Krüss and Schmidt, who expressed the opinion that the latter was considerably below the accepted figure. If this opinion were correct, the atomic weight of the metal obtained by us would presumably differ considerably from the figure obtained for nickel by previous investigators. For this purpose the mirrors obtained were dissolved in aqua regia, evaporated, redissolved in water, and ammonia added until the liquid was coloured blue, filtered, evaporated again, and heated in an open platinum crucible, with access of air, until the weight remained constant. The nickel oxide so obtained was then reduced by hydrogen (made by electrolysis), at a temperature of 500°, until the weight remained constant. In this way the following results were found :—

	Reduced.		Atomic weight. calculated for O = 16.
(1.)	0·2414 gram NiO	0·1896 gram Ni	58·58
(2.)	0·3186 „	0·2503 „	58·64
(3.)	0·3391 „	0·2663 „	58·52

These figures agree sufficiently well with the atomic weight as determined by Russell (= 58·74) to justify the conclusion that the old nickel as we have known it for a great number of years is a simple substance, the atomic weight of which lies very near to the figure hitherto accepted.

LI.—*The Milk of the Gamoose.* (Preliminary Notice.)

By A. Pappel and H. Droop Richmond.

The Egyptian Gamoose or buffalo (*Bos Bubalus*) is the same or very closely allied to that found in India and South Africa, whence it originally came, and in Hungary and Southern Europe; the milk yielded by these animals is distinguished from that of the cow by its white colour and peculiar musk-like smell; this investigation was undertaken to ascertain if any essential chemical difference could be found.

F. Strohmer (*Chem. Centr.*, 1888, 478) has examined the milk of the buffaloes found in Transylvania, and concludes from his single analysis that the chief difference lies in the musk-like smell and the high quantity of fat (over 9 per cent.); he finds no essential difference in the butter, but his examination was very partial; we have not been able to find any other published statements as to the composition of buffalo milk.

All the results we have obtained have been from the milk of animals milked completely dry in our presence, and the figures given in this paper are almost, without exception, averages of from two to sixteen samples; in those determinations where many analyses were made, the maxima and minima are also given.

We find the average composition to be as follows:—

Water	84·10 p. c.			
Fat	5·56 „			
Sugar	5·41 „			Solids not fat 10·34 p. c.
Caseïn	3·26 „	cont. N.	0·511 p. c.	
Albumin	0·60 „	„	0·094 „	
Salts	1·03	Ash	0·850 „	
		Citric acid	0·300 „	
Nitrogenous bases	0·09 „	cont. N.	0·035 „	
	100·05			

The average density at 15·5° (60° F.) was 1·0354.

The calculated figures for fat, sugar, and proteïds respectively, employing the formulæ worked out by one of us ($T = 1·17F + 0·263\frac{G}{D}$, *Analyst*, **14**, 121; and $P = 2·8T + 2·5A - 3·33F - 0·7\frac{G}{D}$, *not yet published*), are—fat, 5·92; sugar, 5·31; proteïds, 4·18; the formula for fat is not applicable in this case, as the mean ratio between sugar, proteïds, and ash does not remain the same as in cows' milk, and consequently the mean density of the solids not fat is altered (compare Vieth, *Analyst*, **13**, 49). The other formula gives very fair results, showing that as far as they affect the density the constituents do not vary much from those of cows' milk.

The variations of the fat were from 7·35 per cent. to 5·15 per cent., and of the solids not fat 10·67 per cent. to 10·07 per cent.

The methods employed in the analysis were as follows:—

Total Solids and Water.—Drying of about 2 grams on the water-bath and in the water-oven to constant weight, a wide platinum dish being used.

Fat.—Adams' method, using the precautions laid down by one of us (*Analyst*, **14**, 121).

Sugar.—By polarisation, after precipitation with acid mercuric nitrate (compare Wiley, *Amer. Chem. J.*, **6**, No. 5; and Vieth, *Analyst*, **13**, 63).

Caseïn.—By precipitation with magnesium sulphate and estimation of the nitrogen by Kjeldahl's method. This includes traces of globulin not estimated (compare Sebelien, (*Zeit. physiol. Chem.*, **13**, 135).

Albumin.—Precipitation by tannin in the filtrate from the caseïn, and estimation of the nitrogen by Kjeldahl's method (compare Sebelien, *loc. cit.*).

Ash.—By calcination at the lowest possible temperature of the total solids.

Citric Acid.—By exact neutralisation of the filtrate used in estimating sugar, collection of the precipitate produced, decomposition with sulphuretted hydrogen, and precipitation of the calcium citrate by boiling the solution obtained.

Nitrogenous Bases.—Calculated from the difference between the total nitrogen and that of the caseïn and albumin (probably of very approximate accuracy only).

The amount of salts was calculated from the ash minus the amount of phosphoric anhydride produced by the combustion of the caseïn plus the amount of citric anhydride calculated equal to the citric acid found: to test the validity of this assumption, the following experiments were made:—

(*a.*) The phosphoric anhydride was estimated in the ash.

(*b.*) The phosphoric anhydride was estimated in the precipitate produced by adding magnesia mixture to the milk.

(*c.*) The phosphoric anhydride was estimated in the precipitate produced by adding magnesia mixture to the milk after it had been mixed with one-third of its bulk of strong ammonia and filtered.

The amounts obtained were:—

(*a*.)	0·276	per cent. P_2O_5.
(*b*.)	0·190	„ „
(*c*.)	0·188	„ „

Taking the average of (*b*) and (*c*), the difference between the two estimations was 0·087 per cent. P_2O_5, the amount calculated equivalent to the citric acid was 0·090 per cent., and the amount equivalent to the caseïn was 0·077 per cent.; these amounts may be taken as sensibly equal, although that calculated from the caseïn does not agree as well as might be desired, and we consider we are justified in calculating the salts existing in the milk as we have done (compare Söldner, *Landw. Versuchs. Stat.*, **35**, 351).

Observations were made on the change of density observed by Rechnagel and Vieth (*Analyst*, **14**, 69) with cows' milk; we took the density as soon as possible after milking, 8 hours after, and 24 hours after, with the following results:—

Increase in 8 hours.	Increase in 24 hours.
0·0006	0·0007

The rise is not so great as that noticed by the above-named observers, and is nearly complete in eight hours, the temperature being from 15—20°; in all cases the highest figure has been taken as the normal one and used in the calculation of the fat, &c.

Gamoose milk, then, differs from that of the cow not only in the high percentage of fat and the musk-like smell, but also in the high amount of solids not fat, this increase being largely due to the sugar.

Various constituents of this milk were prepared and examined.

The Fat.—As already stated, Strohmer did not find any essential difference between the fat of buffaloes' milk and that of cows' milk; in a paper published in the *Revue Egyptienne* No. 1, p. 7, one of us expressed an almost similar opinion, but the examination in each case was only partial; we now find that differences exist, the most striking being the existence of sulphur in such quantities as to instantly blacken a silver dish if saponified therein; we have also found phosphorus as an essential constituent; the quantities being:—

Sulphur	0·05 per cent.
Phosphorus	0·01 „

Of the sulphur a quantity equivalent to 0·01 per cent. was found in the distillate by the Reichert-Wollny method.

The following numbers have been determined:—

Potash required for saponification......	22·04 p.c.	
= Saponification equivalent	254·60	
Insoluble fatty acids	87·50 ,,	
Of which the mean combining weight	270·50	
,, ,, iodine absorption......	41·80 ,,	
,, ,, amount of acids giving lead salts soluble in ether	45·70 ,,	
Of mean combining weight....	297 (?)	
Of iodine absorption	65·10 p.c.	
Iodine absorption of fat	35·00 ,,	
"Oleic" acids calculated from the iodine absorption of fat	35·10 ,,	Mean 35·9
"Oleic" acids calculated from the iodine absorption of fatty acids............	38·10 ,,	
"Oleic" acids calculated from the iodine absorption of fatty acids, of which the lead salts are soluble in ether........	34·60 ,,	
Acids of which the lead salts are soluble in ether and do not belong to the "oleic" series....................	11·10 ,,	
Acids of the "stearic" series	41·80 ,,	
Soluble fatty acids calculated as butyric	6·09 ,,	
Reichert-Wollny figure = about 5·0 p. c. acids as butyric	25·40 c.c. $\frac{N}{10}$ alk.	
Mean combining weight of R.-W. acids	92·30	

Approximate composition—

Butyric acid	80 p. c.
Caproic acid......................	20 ,,

Ratio 4 : 1

Mean combining weight of acids soluble in boiling water but not volatile with steam............................	160 (?)
Glycerol estimated	11·97 p. c.
Glycerol calculated from potash required for saponification..................	12·02 ,,

Very little explanation of the details of the methods employed is necessary, as those of Hehner, Koettstorfer, and Hübl, &c., were followed without modification; the glycerol was estimated in the liquid left in the flask after a Reichert-Wollny determination by the method due to Hehner (*Analyst*, **12**, **44**).

The variations of the insoluble fatty acids found are 87·2 per cent. to 88·8 per cent.

The chief differences we have noticed are:—

(i.) The presence of small quantities of sulphur and phosphorus; we have not yet been able to determine in what form they exist, but are pursuing the investigation.

(ii.) The small Reichert-Wollny figure as compared to the soluble fatty acids; this indicates a quantity of fatty acids soluble in boiling water, but not volatile, much larger than that of cows' milk.

(iii.) The presence of fatty acids giving lead salts soluble in ether, but not belonging to the "oleic" series.

(iv.) The difference in the ratio between butyric and caproic acid: 4 : 1 instead of 2 : 1 (compare Duclaix, *Le Lait*, *Appendix*, and Wollny, *Analyst*, **13**, 8).

Among minor differences are the colour, which is quite white, the more or less tallowy taste and smell, and the invariable presence of free acid in small amount.

From the close agreement between the quantity of glycerol found and that calculated, it is evident that other alcohols do not exist in appreciable quantities.

The method adopted in preparing the butter was to allow the milk to stand for eight hours, to take off the cream, and shake it in a bottle with some water, to wash the resulting butter, and to finally melt it at as low a temperature as possible and filter the fat.

The Sugar.—Milk was precipitated by 4 per cent. of "acid mercuric nitrate," prepared after Wiley's directions (*loc. cit.*), and the clear filtrate was exactly neutralised with caustic soda (phenolphthaleïn being used as indicator), the precipitate being filtered off and used for the preparation of citric acid (see below); through the filtrate was passed sulphuretted hydrogen, and the mercuric sulphide filtered off; the filtrate being then neutral to methyl-orange, but faintly acid to litmus; this was concentrated until all the sulphuretted hydrogen had passed away, a very slight amorphous precipitate separating; after concentration, it was divided into two parts, one being concentrated at 100° until it began to crystallise, and then left in a vacuum over sulphuric acid, and to the other, two volumes of alcohol were added, and this was concentrated in a vacuum over sulphuric acid; each of the sugars obtained in this way was recrystallised three times and the following figures determined:—

	$[\alpha]_D$.	κ.	δ.	$\frac{\kappa}{[\alpha]_D}$.
From water....	48·6°	73·6	3·94	1·514
From alcohol ..	48·7	73·8	3·94	1·515

δ is the influence of 1 gram in 100 c.c. on the density at 15·5°, the density of water being taken as 1000.

The mother liquors mixed gave:—

$[\alpha]_D$.	κ.	$\frac{\kappa}{[\alpha]_D}$.
50·2°	77·3	1·54

The figures for the rotatory and cupric-reducing powers are somewhat doubtful as absolute numbers, as the quantity of salts, chiefly sodium nitrate in this solution, which very largely exceeded the sugar, rendered the exact determination of the amount of sugar difficult, but the ratio between the two figures is sufficiently close to that given by the pure sugars to indicate that only one sugar is contained in the milk.

This sugar gives dextrose only on hydrolysis, as is shown by the following figures:—

$[\alpha]_D$.	κ.	$\frac{\kappa}{[\alpha]_D}$.
53·1°	100·5	1·893

It undergoes inversion with great readiness, as is shown by a determination of the cupric-reducing and rotatory power in a solution which was heated for five minutes with a trace of acid (not more than 0·1 per cent.), which had accidentally fallen into the solution:—

$[\alpha]_D$.	κ.	δ.	$\frac{\kappa}{[\alpha]_D}$.
52·3°	96·3	3·93	1·841

These figures approach those of dextrose, and correspond almost exactly to a mixture of 87 per cent. of dextrose with 13 per cent. of this sugar.

This sugar is not identical with that of cows' milk, and by permission of His Highness Mahommed Tewfik Pacha, Khedive of Egypt, we propose to call it "tewfikose."

As we have found that animals so closely allied as the cow and the buffalo give in their milk different sugars, we consider that it will be worth while to examine more closely than has hitherto been done the milk of other animals, and we propose to undertake the examination of the animals which are found in Egypt.

The Albuminoids do not appear to differ very materially from those of cows' milk; we have not been able to obtain as high a percentage of nitrogen as from cows' milk (15·7 per cent.); but, as our results are not constant, we refrain from giving any figures at present; the amount of phosphorus appears to be rather higher.

Citric Acid.—We prepared citric acid from the milk by a method substantially the same as that used in the estimation, and have characterised the citric acid; a determination of calcium in the calcium salt gave:—

Ca ...... 24·4 per cent. Theory ...... 24·1 per cent.

We are now continuing the investigation, and wish to reserve to ourselves the work of determining the composition of the various constituents of gamoose milk, but we invite other chemists who may have the opportunity to assist us in determining the purely analytical figures in order to establish limits.

We have to express our thanks to Mr. Hussein Off for assistance in our work.

Khedival Laboratory,
Cairo.

LII.—*The Interaction of Iodine, Water, and Potassium Chlorate.*

By Henry Bassett.

Having occasion some three or four years ago to prepare some quantity of iodic acid, I made use of the excellent method given by Millon at the beginning of his elaborate paper on iodic acid and iodates (*Ann. Chim. Phys.* [3], 9, 400, 1843); but the results of the first trial were so widely different from his description as to necessitate further experiments. The usual accounts of the process, repeated pretty uniformly in most books, represent the action as a direct displacement of the chlorine by an equivalent of iodine; but my experiments lead to such a different interpretation as to induce me to bring them before the Society.

The directions given by Millon are as follows:—

80 parts of iodine,
75 " potassium chlorate,
1 " nitric acid,
400 " water,

"are placed in a flask of sufficient capacity. The flask is heated to boiling, and removed from the lamp as soon as the chlorine begins to be abundantly liberated."

In the first experiment made, 75 grams of potassium chlorate were dissolved in 400 c.c. of water with 1 c.c. of nitric acid, and heated to about 80°. Then the prescribed 80 grams of iodine were added, not all at once, but by degrees. Under these circumstances, the iodine dissolved slowly at first, but quicker and quicker at each addition till the whole had disappeared, but without any evolution of chlorine beyond a very slight indication at the last, when the liquid was nearly boiling. At each addition of iodine, a peculiar greenish-yellow colour appeared in the liquid, which very soon vanished—no doubt, due to chlorous acid.

Finding that the liquid would still take up iodine, I added gradually 30 grams more, when it became of a permanent orange-yellow colour. Then added more chlorate till the colour disappeared, the quantity required being 14 grams. The total proportions used were, therefore, 110 grams of iodine and 89 grams of chlorate.

On cooling, a large quantity of well-crystallised biniodate of potassium was deposited. On boiling down the mother liquor from this, a steady effervescence of chlorine began when somewhat concentrated, accompanied when getting nearly dry by brownish vapours of iodine chloride.

The salt dissolved in water, and precipitated hot by barium nitrate, gave a large quantity of crystalline barium iodate. I must here mention a very curious fact already noticed by Gay-Lussac in his magnificent research on iodine (*Annalen*, **91**, 5, 1814). The barium iodate, after drying over sulphuric acid, when heated in the water-oven, loses 1·8 per cent. of hygroscopic water, and when taken out and exposed to the air, the crystals are seen under a magnifier to be in a state of violent agitation and disruption, throwing up a fine powder, which settles all round the mass, looking as if a sublimate had condensed there. Gay-Lussac refers to this as occurring during drying, but it really happens on cooling after drying, and is accompanied by an increase of weight, and in some hours all the original loss is made up. Some specimens do not behave in this way at all, and others only in a less degree.

The next experiment was made with—

6	grams of	iodine,
6	„	chlorate,
30	„	water,
0·03	„	iodic acid,

mixed all at once, and heated up gradually to 50—60°, when solution began—kept at 65° till all the iodine dissolved, which took about two hours, the action being very slow at this temperature. No chlorine was given off.

Next day the solution was poured off, and the crystalline deposit washed with a little water. The solution was found to be very strongly acid. Neutralised with barium hydrate, filtered from the small quantity of barium iodate precipitated, and made up to 200 c.c.

20 c.c. precipitated with silver nitrate gave 0·475 gram AgCl.

20 c.c. evaporated to dryness, and heated strongly to complete decomposition, redissolved in water, and precipitated with silver nitrate, gave 0·566 gram AgCl.

Now 566 : 475 : : 6 : 5·04, indicating that one-sixth of the potassium chlorate remains in excess unacted upon by the iodine used. This was confirmed by saturating filter-paper with the solution, and drying, when it burnt with deflagration.

Experiment 3.

6 grams of iodine,
5 „ chlorate,
30 „ water,
1 drop of nitric acid,

mixed all at once, and heated to 80°. The iodine rapidly dissolved without evolution of chlorine, and the resulting solution was colourless. Then added 0·1 gram of iodine, which dissolved with yellow colour, which soon disappeared. Another decigram of iodine gave the same result, and again a third, but, on adding more, the yellow colour was permanent.

The equation indicated by these experiments is—

$$6I_2 + 10KClO_3 + 6H_2O = 6KHI_2O_6 + 4KCl + 6HCl,$$

which leads exactly to the proportions—61 parts iodine to 49 parts potassium chlorate, which are confirmed by the quantities arrived at in the first experiment by a purely tentative method, viz., 110 grams of iodine and 89 grams of chlorate.

Now 61 : 49 : : 110 : 88·4.

Experiment 4.

6·1 grams of iodine,
4·9 „ chlorate,
30 „ water,
1 c.c. of dilute nitric acid,

mixed, and heated to 80° in a long-necked flask. Colourless solution formed with no evolution of chlorine. Added water, and made up to 250 c.c. when cold. 50 c.c. of this gave on titration numbers corresponding to 2·548 grams Na_2CO_3 for the whole solution, that is, for the product from 4·9 grams of potassium chlorate (allowing, of course, for the 1 c.c. dilute nitric acid). The equation above requires 2·544 grams.

After the above experiments were finished, I happened to refer to the account of the process given in Schützenberger's *Traité de Chimie Générale*, which concludes as follows:—

"If, instead of heating, we operate in the cold, we may succeed in dissolving all the iodine without liberation of chlorine. In fact, the displaced chlorine oxidises the iodine in presence of water, yielding iodic and hydrochloric acids—

$$\text{"}5Cl_2 + 5H_2O + I_2 = 10HCl + I_2O_5,$$

from which it follows that we may diminish the proportion of chlorate, for we have—

$$\text{"}10KClO_3 + 6I_2 + 5H_2O = 10HCl + 10KIO_3 + I_2O_5.\text{"}$$

It will be seen that this equation amounts to much the same thing as that previously given, and I was at first under the impression that there was perhaps nothing new in my results. Finding, however, on making the experiment that no action whatever happened in the cold even after several weeks, I last year determined to look into the matter more fully.

In order to account for the evolution of chlorine which Millon must undoubtedly have observed, some experiments were made exactly as described, that is, by mixing the ingredients all at once, and heating to boiling. Under these circumstances, when using quantities of 40 or 50 grams of iodine, it was found that at a certain point a violent action was set up, with evolution of some quantity of chlorine, accompanied, of course, by much vapour of iodine and iodine chloride; but this only occurred after a considerable quantity of iodine had been dissolved, and is, doubtless, owing to the rapid formation of iodic and hydrochloric acid in the dense mass of iodine at the bottom of the flask causing a secondary action:—

$$HIO_3 + 5HCl = 3H_2O + ICl + 2Cl_2,$$

This action was soon checked on reducing the temperature by dipping the flask in water for a short time, but the dissolution of the iodine still went on rapidly without further evolution of chlorine.

This is an important point, as it is obvious that if the evolution of chlorine were due to direct displacement by the iodine as usually represented, it would begin and continue concurrently with the more or less rapid solution of the latter.

At the commencement of Millon's paper, already referred to, he mentions incidentally a former paper on the subject, which does not seem to be so well known. This is "On the Action of Iodine on

Potassium Chlorate" (*Compt. rend.*, **12**, 258, 1841), and I make the following short extracts from it:—

"Potassium chlorate is dissolved in three or four times its weight of water, and heated to boiling. Iodine then added dissolves in considerable quantity, the solution remaining colourless so long as not much more than one equivalent to one of chlorate is added. After this point, the liquid becomes yellow, then brown. The final result is neutral potassium iodate, and more or less iodised chloride of iodine. Evaporation to dryness gets rid of the latter, leaving pure potassium iodate."

Then follow some details, and a very curious explanation of the probable action, concluding:—

"The reaction may be represented thus—

$$\text{"}5KClO_3 + 6I = 5KIO_3 + ICl_5.\text{"}$$

He then refers to "the interesting modification of the reaction induced by the addition of a few drops of acid to the mixture . . . . . . an action much more lively than that occurring between iodine and chlorate alone . . . . . . at the same time, an abundant disengagement of chlorine takes place, and on afterwards evaporating to dryness a very pure potassium iodate is obtained."

Further on, he says, "the chloride of iodine which is an essential product of the first reaction . . . . . . is scarcely formed at all under the influence of the nitric acid, so rapid is the evolution of chlorine."

Lastly.—"To prove the exactness of these reactions . . . . . . 10 grams of dry potassium chlorate, treated by a sufficient quantity of iodine and a drop of nitric acid, and evaporated to dryness, gave a residue of 17·3 grams of perfectly white potassium iodate—theory requiring 17·4 grams.

"1·805 grams of this decomposed by heat gave 1·389 grams potassium iodide—theory requiring 1·399."

No equation is given for the modified reaction.

Experiments were then made without the addition of acid, and the first point noticed was that in many cases, but not always, the iodine coloured the liquid brown without any further action taking place for a considerable time, even when boiled. In one case, no change occurred for more than an hour at 80°, but then the liquid became suddenly colourless, and the solution of the iodine went on rapidly. The introduction of the least possible trace of acid, however, always caused instantaneous decolorisation.

Experiments made side by side, with and without addition of acid, showed no difference in behaviour after the action was once started.

I then proceeded to the examination of the results obtained by evaporating the solution to dryness. A number of preparations were made, using always 6·1 grams of iodine, 4·9 grams of chlorate, and about 40 c.c. of water (without any addition of acid).

These mixtures were placed in bulb-tubes, the necks drawn off and sealed, and then heated in a water-bath at from 80° to 100° with occasional agitation, till all iodine had disappeared, and the solutions were nearly or quite colourless. On cooling, a considerable quantity of white salt was deposited. In no case was any chlorine found on opening the tubes. The contents of each bulb were then dissolved in cold water, and made up to 500 c.c.

Three of these original solutions were titrated cold with sodium carbonate, using methyl-orange as indicator, and gave numbers corresponding to 2·536, 2·533, and 2·538 grams of Na_2CO_3 for the whole solution, confirming the first experiment for the total acidity.

All subsequent analyses were calculated in the same way to correspond to 4·9 grams $KClO_3$.

The solutions were evaporated to dryness on the water-bath in flat dishes, in quantities of 50 or 100 c.c. When approaching dryness, chlorine was given off, and also some chloride of iodine, which gave a yellow colour to the residue. On the addition of a few drops of water, again drying, and repeating this process 5 or 6 times, a perfectly white, odourless residue was obtained, which was dried in the water-oven till the weight was constant.

Fifteen experiments, of which the extreme results only varied 1 per cent., the majority being much closer, gave a mean weight of 9·919 grams for 4·9 grams $KClO_3$.

Supposing the residue to be pure potassium iodate, it should weigh 8·560 grams, but on examination it was found to be acid, and to contain chlorine.

On titration, seven closely agreeing experiments gave a mean result corresponding to 1·160 grams Na_2CO_3 for 4·9 grams $KClO_3$.

The chlorine and iodine were determined as follows:—

To a dilute solution, pure sodium bisulphite was added gradually to slight excess, that is, till the iodine, liberated at first, disappeared. Then added silver nitrate and a sufficient quantity of nitric acid and heated moderately with stirring. The resulting precipitate of $AgI + AgCl$ was then washed, dried, and weighed.

Two experiments gave weights corresponding to 12·857 grams and 12·900 grams for 4·9 grams $KClO_3$.

Further experiments were then made as follows:—

The mixed precipitates obtained as above were, after washing, rinsed into a beaker, and digested at a gentle heat with hydrochloric acid and potassium chlorate for an hour or two. Then added hot water, boiled for a few minutes, and allowed to stand till next day, when the liquid was quite bright. Then washed, dried, and weighed the residue of AgCl + AgCl.

Three experiments gave weights corresponding to 8·871 grams, 8·865 grams, and 8·900 grams for 4·9 grams $KClO_3$.

The method is very satisfactory with a little care; the most important precaution being to avoid making the reduction in a strong light, for reasons to which I need not now refer.

These results lead to the following equation, expressing the decomposition on evaporating the original solution to dryness :—

$$12KHI_2O_6 + 8KCl + 12HCl = 11KHI_2O_6 + 9KCl + 6H_2O \\ + ICl + ICl,HCl + 4Cl_2.$$

The theoretical numbers calculated from this for 4·9 grams $KClO_3$ are :—

	Grams.	Mean found. grams.
Weight of the residue $11KHI_2O_6 + 9KCl$....	9·921	9·919
Na_2CO_3 required to neutralise do.	1·166	1·160
Mixed silver salts from do. = $22AgI + 9AgCl$	12·923	12·879
Do. after chlorination = $22AgCl + 9AgCl$ ..	8·897	8·879

The next step was to try the effect of higher temperatures on the residue from the water-bath. It was found impossible to arrive at any definite results by heating in dishes on a sand-bath, and an air-bath at a uniform temperature of 250° was then tried, but the heat was not sufficient.

Several experiments were then made in bulb-tubes plugged with asbestos. The decomposition showed three well marked stages. At first the bulb was filled with brown vapours of chloride of iodine, soon replaced by violet iodine vapour, which in its turn was expelled by large quantities of oxygen.

On examination of the final residue it was found invariably to contain about 3 per cent. of potassium chloride, the separation of the iodine being made directly by palladium so as to avoid any doubt which might arise from the employment of an indirect method. I refrain from giving any symbolical expressions for these final decompositions, though I believe that the analytical results obtained give reasonable indications of such expressions; but they are rendered inexact by several causes, among which I may mention the corrrosion of the glass by the fused salt, which was found to contain silica, and also by a secondary action of which I obtained distinct evidence, and to which I hope to have occasion to refer in a future communication.

My best thanks are due to Mr. E. Fielding for his able assistance in the earlier experiments, and to Mr. F. A. Manning for the use of his laboratory.

LIII.—*The Action of Heat on the Chlorides and Hydroxides of Mixed Quaternary Ammonium Compounds.*

By N. Collie, Ph.D., and S. B. Schryver, B.Sc.

The object of the following work was to obtain, if possible, a general method for preparing the mixed tertiary amines. One of us (Collie, Trans., 1888, 714—726) has found that by the action of heat upon the quaternary phosphonium compounds various mixed tertiary phosphines could be prepared, and the following results show distinctly a marked analogy between the compounds of nitrogen and those of phosphorus.

Hofmann has already pointed out that when the hydroxides of mixed quaternary ammonium compounds containing ethyl-groups are heated, invariably one of the ethyl-groups is eliminated in the form of ethylene (Hofmann, *Annalen*, **78**, 282—284, and **79**, 12—15):—

$$(C_2H_5)_3(C_5H_{11})N\cdot OH = (C_2H_5)_2(C_5H_{11})N + C_2H_4 + H_2O.$$
$$(C_2H_5)_2(CH_3)(C_5H_{11})N\cdot OH = (C_2H_5)(CH_3)(C_5H_{11})N + C_2H_4 + H_2O.$$

And Lossen (*Annalen*, **81**, 376—383) confirms the results of Hofmann with regard to the action of heat on the mixed ethylmethylammonium hydroxides.

He has also tried the action of heat on some of the corresponding chlorides with the following results:—

$$(C_2H_5)_3(CH_3)NCl = (C_2H_5)_2(CH_3)N + C_2H_5Cl,$$
$$\text{also } (C_2H_5)_3N + CH_3Cl.$$
$$(C_2H_5)(CH_3)_3NCl = (C_2H_5)(CH_3)_2N + CH_3Cl.$$

But none of the mixed tertiary amines thus prepared was obtained in the pure state; both Hofmann and Lossen being content to convert them back again into quaternary ammonium compounds, and analyse the platinum salts.

There was therefore, no doubt that mixed tertiary amines could be prepared both from the hydroxides and chlorides of the mixed quaternary ammonium compounds, and a wider field for investigation was opened with the ammonium compounds than with the corresponding phosphonium-derivatives. For the quaternary phosphonium chlorides alone yielded mixed tertiary phosphines when decomposed by heat:—

$$(C_2H_5)_3(C_5H_{11})PCl = (C_2H_5)_2(C_5H_{11})PHCl + C_2H_4,$$

whilst the hydroxides, owing to the great affinity of phosphorus for oxygen, always gave tertiary phosphine oxides:—

$$(C_2H_5)_3(C_7H_7)N{\cdot}OH = (C_2H_5)_3PO + C_7H_8.$$

In the present work, we have always used as a starting point either trimethylamine or triethylamine, and from these tertiary amines we have prepared the quaternary ammonium compounds by heating an alcoholic solution of the amine with the iodide or chloride of primary, secondary, or tertiary hydrocarbon radicles of the C_nH_{2n+1} series. The action of heat on the quaternary ammonium compounds containing the radicles allyl, benzyl, and phenyl has also been studied.

The trimethylamine and triethylamine were prepared by the action of heat on tetramethylammonium and tetrethylammonium chlorides; these salts decompose quantitatively when heated as follows:—

$$R_4NCl = R_3N + RCl.$$

The free amine was collected in hydrochloric acid, and the hydrochlorides thus obtained were concentrated to the consistency of a syrup. Portions of the salt were decomposed from time to time with saturated caustic soda solution, and the free tertiary amine distilled into dry alcohol.

I.—MIXED QUATERNARY AMMONIUM COMPOUNDS PRODUCED FROM TRIMETHYLAMINE.

The Action of Heat on Trimethylethylammonium Chloride.

This salt was prepared from a strong alcoholic solution of trimethylamine by adding ethyl iodide, and converting the iodide thus formed into the chloride. An analysis of the iodide was made (iodine found 59·1 and 58·9 per cent.; theoretical iodine = 59·0 per cent.). A small quantity of the chloride was also converted into the platinum salt and analysed (platinum found 33·1 per cent.; theoretical, 33·3 per cent. Pt). The action of heat on this mixed chloride has already been tried by Lossen, who found that it decomposed as follows:—

$$(CH_3)_3(C_2H_5)NCl = (CH_3)_2(C_2H_5)N + CH_3Cl.$$

We were, however, anxious to obtain, if possible, the mixed tertiary amine pure, and so repeated his experiment.

A preliminary experiment was first tried with 4·3 grams of the solid chloride. At a temperature above 300° the salt decomposed without fusion. The products were passed into a U-tube containing hydrochloric acid (to absorb the amine) and the gas which was also evolved was collected above mercury. 800 c.c. were obtained, the theoretical amount being about 790 c.c. This gas was evidently a chloride, for it burnt with a green flame, and on shaking with water slowly dissolved. An analysis showed that it was not pure methyl chloride, but contained probably ethyl chloride as well, for 10·2 c.c., after explosion with oxygen, gave 11·5 c.c. of carbon dioxide.

A much larger quantity of the chloride was then subjected to the action of heat. The free amines were absorbed in hydrochloric acid, and the solution of the hydrochlorides were evaporated over a water-bath nearly to dryness. The resulting liquid was then transferred to a distilling flask, and a saturated solution of caustic soda added. An oily liquid separated, which by a very gentle heat was distilled over into a fractionating flask containing solid caustic soda, and surrounded with ice. On fractionating, the dry amines were split into three portions:—

I. Under 25°, nearly pure trimethylamine.
II. From 25° to 45°, a mixture of trimethylamine and dimethylethylamine.
III. From 45° to 49°, nearly pure dimethylethylamine.

These three fractions were examined in the following way:—

I. Ethyl iodide was added to the alcoholic solution of the amine and the trimethylethylammonium iodide was analysed (iodine found 59·1 per cent.; theoretical iodine = 59·0 per cent.).

II. This fraction (about 9 grams) was added to an alcoholic solution of 3 grams of ethyl iodide. By thus using a quantity of ethyl iodide only sufficient to combine with a small portion of the amine, it was thought that a separation of the two amines (dimethylethylamine and trimethylamine) might be effected, the iodide of ethyl probably uniting with the trimethylamine most readily. This was found to be the case. After the unacted on tertiary amines had been recovered and dried, on refractionating them, a further quantity was obtained boiling from 45—50°.

III. The third fraction was mixed with the portion boiling from 45—50° obtained from fraction II, and redistilled. The part which boiled from 45—47° was analysed and proved to be dimethylethyl amine:—

0·2455 gram substance gave 0·5945 gram CO_2 and 0·337 gram H_2O.
0·240 gram substance gave 40·1 c.c. of nitrogen at 14° and 752 mm.

	Calculated for $(CH_3)_2(C_2H_5)N$.	Found. I.	Found. II.
C	65·75	66·04	—
H	15·07	15·25	—
N	19·17	—	19·41

This boiling point (45—47° C.) differs from the boiling point (39—41° C.) of the specimen of dimethylethylamine prepared from triethylamine (see p. 780). The remainder, therefore, of this third fraction was again carefully dried and distilled; eventually nearly the whole was found to boil between 42—43° C., from which we are inclined to believe that the true boiling point lies about 40—42° C.

The decomposition, therefore, of the trimethylethylammonium chloride, although yielding substantially the mixed tertiary amine, still gives at the same time trimethylamine:—

$$(CH_3)_3(C_2H_5)NCl = (CH_3)_2(C_2H_5)N + CH_3Cl,$$
$$(CH_3)_3(C_2H_5)NCl = (CH_3)_3N + C_2H_5Cl.$$

This result differs from that obtained by Lossen, who gives as the products of decomposition only dimethylethylamine and methyl chloride.

The Action of Heat on the Trimethylethylammonium Hydroxide.

This compound Lossen has shown to decompose into water, ethylene, and trimethylamine. But after the results obtained with the chloride, we thought it worth while to repeat this experiment.

The hydroxide was prepared from the iodide by treating an aqueous solution of the salt with oxide of silver. After evaporation over a water-bath, the hydroxide was submitted to the action of heat in an ordinary distilling flask, connected with the apparatus which we invariably used during this work, namely, a U-tube filled with hydrochloric acid to absorb the free amine, and surrounded with cold water; and a gasometer to collect any gas which might be formed during the experiment. The hydroxide did not decompose till the temperature had risen above 200°; a large quantity of gas was produced which proved to be pure ethylene. It burnt with a luminous flame and was completely absorbed by bromine, giving dibromethylene (b. p. 131—132°).

The solution of the tertiary amine in hydrochloric acid was then evaporated nearly to dryness, and the concentrated solution treated with a saturated solution of caustic soda. The free base thus liberated was distilled over into dry alcohol, and on addition to this of ethyl iodide, a precipitate was at once obtained. This salt was converted into the platinichloride, and from the analysis was shown to be pure iodide of trimethylethylammonium :—

0·6014 gram salt gave 0·2006 gram Pt = 33·35 per cent. Pt in $[(CH_3)_3(C_2H_5)NCl]_2PtCl_4$ = 33·38 per cent.

Hence the decomposition of the base may be represented by the equation :—

$$(CH_3)_3(C_2H_5)N\cdot OH = (CH_3)_3N + H_2O + C_2H_4.$$

This result agrees with that obtained by Lossen.

Action of Heat on the Chloride and Hydroxide of Trimethylpropylammonium.

The chloride was produced by heating in a sealed tube chloride of propyl and a strong alcoholic solution of trimethylamine. The contents of the sealed tube, on evaporation over a water-bath, left a deliquescent mass, which was dissolved in water and treated with silver oxide; this solution smelt of trimethylamine, which had probably been formed by the propyl chloride being decomposed into hydrochloric acid and propylene :—

$$(CH_3)_3N + C_3H_7Cl = (CH_3)_3NHCl + C_3H_6.$$

The whole of the contents of the tube were therefore treated with oxide of silver and the solution evaporated to drive off the free trimethylamine. After filtering, one half was neutralised with hydrochloric acid, and the other half was decomposed by the action of heat. A small portion of the chloride was converted into the platinichloride by adding excess of chloride of platinum and alcohol, and the precipitated salt was washed with alcohol and ether and analysed without recrystallising.

0·303 gram salt gave 0·096 gram Pt = 31·68 per cent. Pt in $[(CH_3)_3(C_3H_9)NCl]_2PtCl_4$ = 31·86 per cent.

The remainder of the chloride was evaporated to dryness, and heated in a flask connected with the usual apparatus for collecting the free amine and also any gas which might be formed.

Chloride of methyl collected in the gasometer and a few drops of a liquid, presumably chloride of propyl, were noticed in the hydrochloric acid. The free tertiary amine, which was obtained from this hydrochloric acid solution, was converted by means of methyl iodide into the quaternary ammonium compound and directly analysed.

0·5525 gram took 26·936 c.c. $\frac{N}{10}$ $AgNO_3$ solution = 61·92 per cent. iodine.

	Calculated for		
	$(CH_3)_3(C_3H_7)NI$.	$(CH_3)_4NI$.	Found.
Iodine......	55·45	63·18	61·92

thus proving that the decomposition took place in probably two ways:—

$$(CH_3)_3(C_3H_7)NCl = (CH_3)_3N + C_3H_7Cl,$$
$$(CH_3)_3(C_3H_7)NCl = (CH_3)_2(C_3H_7)N + CH_3Cl.$$

The action of heat on the hydroxide yielded nearly the same results. A gas was produced which was completely absorbed by bromine, yielding a liquid which was not pure dibromethylene or dibromopropylene, its boiling point rising steadily from 130° to 140°. The hydrochlorides of the tertiary amine were converted into the quaternary ammonium compound by treatment with methyl iodide and the salt analysed.

0·5315 gram salt took 25·74 c.c. $\frac{N}{10}$ $AgNO_3$ = 61·51 per cent. iodine,

showing that in this case, as well as in that of the chloride, the chief product of the reaction was trimethylamine, while small quantities of dimethylpropylamine were also formed. Owing to the small quantity of the free dimethylpropylamine which we obtained, we were unable to get it in a pure state.

The Action of Heat on the Chloride and Hydroxide of Trimethylisopropylammonium.

Isopropyl iodide (prepared from glycerine) was added to a solution of trimethylamine in alcohol; after a short time, white, needle-shaped crystals of iodide of trimethylisopropylammonium iodide separated; in order to complete the reaction the solution was finally warmed. The aqueous solution of this iodide when treated with oxide of silver gave free trimethylamine, and in this respect resembled the salt obtained in the previous experiment with propyl chloride and trimethylamine; the whole was therefore treated with oxide of silver. The excess of trimethylamine was boiled off and part of the hydroxide was reserved for heating, whilst part was neutralised with hydrochloric acid to form the chloride.

An analysis of the platinichloride gave the following numbers:—

0·4555 gram salt gave 0·1460 gram Pt = 32·05 per cent. Pt in $[(CH_3)_3(C_3H_7)NCl]_2PtCl_4$ = 31·86 per cent.

The chloride, on heating, decomposed yielding a gas which was not pure chloride of methyl, as about 2 per cent. was absorbed by bromine. Chloride of propyl was also formed. The free amine was treated in the usual manner with methyl iodide and then converted into the platinichloride :—

0·135 gram salt gave 0·0461 gram Pt = 34·14 per cent.

	Calculated for $[(CH_3)_4NCl]_2PtCl_4$.	Calculated for $[(CH_3)_3(C_3H_7)NCl]PtCl_4$.	Found.
Pt........	35·07	31·86	34·14

The salt therefore decomposes as follows :—

$$(CH_3)_3(C_3H_7)NCl = (CH_3)_3N + C_3H_7Cl,$$
$$(CH_3)_3(C_3H_7)NCl = (CH_3)_2(C_3H_7)N + CH_3Cl.$$

The hydroxide decomposes in a similar manner. Propylene was formed, mixed with traces of ethylene. And the tertiary amines, when converted into iodides and then into platinichlorides of the quaternary ammonium compounds, gave on analysis :—

0·4262 gram salt gave 0·1496 gram Pt = 15·10 per cent. Pt,

which showed that the decomposition was almost completely into trimethylamine, &c. :—

$$(CH_3)_3(C_3H_7)N{\cdot}OH = (CH_3)_3N + C_3H_6 + H_2O.$$

The Action of Heat on the Chloride and Hydroxide of Trimethylisobutylammonium.

The chloride of trimethylisobutylammonium was prepared by heating isobutyl chloride and an alcoholic solution of trimethylamine in a sealed tube. A small portion of the salt thus obtained, when treated with oxide of silver, gave a trace of free trimethylamine. Isobutyl chloride therefore resembles the haloïd compounds of propyl when heated with trimethylamine, being decomposed into butylene and hydrochloric acid.

The whole of the chloride obtained from the sealed tube reaction was converted into the hydroxide and evaporated over the water-bath to purify it from the hydrochloride of trimethylamine. It was then divided into two halves; one was neutralised with hydrochloric acid, and the other was decomposed by heat.

A small quantity of the chloride was converted into the platinum double chloride and analysed :—

0·156 gram salt gave 0·0475 Pt = 30·45 gram per cent. Pt in $[(CH_3)_3(C_4H_9)NCl]_2PtCl_4$ = 30·46 per cent.

The remainder was evaporated to dryness and heated; it decomposed at a low temperature (below 200°) and yielded a considerable quantity of methyl chloride. The solution of tertiary amines in hydrochloric acid was treated with caustic soda and the amines distilled into alcohol. Methyl iodide was then added, and the iodides were converted into the platinichlorides. The platinum salt was fractionally crystallised.

Fraction I.—0·3019 gram Pt salt gave 0·0931 Pt = 30·83 per cent.
Fraction II.—0·2837 gram Pt salt gave 0·0871 Pt = 30·70 per cent.
Pt in $[(CH_3)_3(C_4H_9)NCl]_2PtCl_4$ = 30·46 per cent.

The decomposition is, therefore, almost wholly into the mixed amine and methyl chloride,

$$(CH_3)_3(C_4H_9)NCl = (CH_3)_2(C_4H_9)N + CH_3Cl.$$

It may be mentioned that the chloride of trimethylisobutylammonium seems to be decomposed slightly when boiled with caustic soda solution; free dimethylisobutylamine is formed, and can be recognised by its smell.

The hydroxide seems to decompose in a manner analogous to the chloride; only traces of a permanent gas are formed, which are absorbed by bromine, while the tertiary amine was proved to be dimethylisobutylamine.

The tertiary amine was treated with methyl iodide and then converted into the platinum double chloride and analysed.

0·423 gram salt gave 0·130 gram Pt = 30·73 per cent., and the following equation represents the decomposition:—

$$(CH_3)_3(C_4H_9)N{\cdot}OH = (CH_3)_2(C_4H_9)N + CH_3{\cdot}OH.$$

The Action of Heat on the Chloride and Hydroxide of Trimethylisoamylammonium.

When isoamyl chloride and alcoholic solution of trimethylamine are heated together to 120° in a sealed tube, complete combination occurs, and on cooling, the tube is filled with a white, crystalline mass. A sample was converted into the double platinichloride and analysed. 0·4750 gram gave 0·1380 gram Pt = 29·0 per cent. Pt in $[(CH_3)_3(C_5H_{11})NCl]_2PtCl_4$ = 29·1 per cent. The chloride itself is a white, deliquescent solid, which, when heated to a temperature above 200°, decomposes into methyl chloride and the mixed tertiary amine,

$$(CH_3)_3(C_5H_{11})NCl = (CH_3)_2(C_5H_{11})N + CH_3Cl.$$

After the free amine had been liberated from the hydrochloride and dried over solid caustic soda, it nearly all boiled between 113° and 114°. An analysis gave the following numbers:—

0·137 gram substance gave 0·368 gram CO_2 and 0·188 gram H_2O.
0·231 gram substance gave 24·5 c.c. nitrogen at 14° C. and 742 mm.

	Calculated for $(CH_3)_2(C_5H_{11})N$.	Found.	
		I.	II.
C........	73·04	73·25	—
H........	14·78	15·27	—
N........	12·17	—	12·17

As there were only traces of trimethylamine formed, the decomposition of this chloride of trimethylamylammonium seems to be almost completely into methyl chloride and the mixed tertiary amine.

The decomposition of the hydroxide is, however, different, for only a very small quantity of gas was produced when the hydroxide was heated, while an oily liquid condensed in the hydrochloric acid tube used for absorbing the tertiary amine. This liquid possessed the smell of amylene, and boiled almost at ordinary temperatures; it was treated with bromine, and the dibromide thus produced boiled with decomposition between 173° and 180°. This happens with the amylene obtained from fusel oil, the bromide boiling from 170° to 180° with partial decomposition.

The hydrochloric acid solution of the tertiary amines was evaporated, and then treated with concentrated solution of caustic soda; a large quantity of trimethylamine was liberated, which was boiled off, leaving only a very small amount of the mixed tertiary amine. The amine was extracted with ether and fractionated; only a very small quantity was obtained boiling from 110° to 115°. This was treated with methyl iodide and converted into the platinum salt. The percentage of platinum found was 29·0, while the amount required by theory is 29·1. Hence the reaction is chiefly

$$(CH_3)_3(C_5H_{11})N{\cdot}OH = (CH_3)_3N + C_5H_{10} + H_2O,$$

while a small quantity decomposes as follows:—

$$(CH_3)_3(C_5H_{11})N{\cdot}OH = (CH_3)_2(C_5H_{11})N + CH_3{\cdot}OH.$$

As a considerable amount of the dimethylamylamine had been obtained, an attempt was made to unite it with another molecule of amyl chloride, but even after heating for many hours at 120°, no combination occurred. The iodide of amyl was, therefore, employed, but even then the substances had to be heated in a sealed tube before combination would take place. The contents of the sealed tube was converted into the chloride, and a small portion precipitated with platinum chloride. This salt melted below the temperature of boiling water, but could be dissolved in boiling water. On recrystallisation, it proved by analysis to be the dimethyldiamylammonium platinichloride.

0·210 gram substance gave 0·053 gram Pt = 25·23 per cent.
Pt in $[(CH_3)_2(C_5H_{11})_2NCl]_2PtCl_4$ = 25·00 per cent.

The remainder of the chloride was heated. It was found to decompose into methyl chloride and diamylmethylamine, which latter substance, after treating with methyl iodide and being converted into the platinum salt, gave 25·38 per cent. Pt, showing that the decomposition was similar to that of the dimethylamylammonium chloride, and is represented by the following equation:—

$$(CH_3)_2(C_5H_{11})_2NCl = (C_5H_{11})_2(CH_3)N + CH_3Cl.$$

The Action of Heat on the Chloride and Hydroxide of Trimethylallylammonium.

When allyl iodide is added to an alcoholic solution of trimethylamine, the reaction takes place immediately. The iodide thus formed is a deliquescent solid, which is easily soluble both in alcohol and in water.

It was converted completely into the hydroxide. The solution of the hydroxide was divided into two portions; one was neutralised with hydrochloric acid, and the other half evaporated to dryness and heated.

The decomposition of the base did not, however, yield very satisfactory results. The chief tertiary amine produced was undoubtedly trimethylamine, while the allyl radicle was decomposed, yielding considerable quantities of acroleïn, which was recognised by its smell and the power it possessed of reducing a silver solution. A very small quantity of dimethylallylamine was, however, formed, for after treating with methyl iodide and converting in the usual manner into the platinichloride, it gave the following result:—

0·1602 gram substance gave 0·514 gram Pt = 32·08 per cent.
Pt in $[(CH_3)_3(C_3H_5)NCl]_2PtCl_4$ = 32·07 per cent.; the chief reaction is therefore

$$(CH_3)_3(C_3H_5)N{\cdot}OH = (CH_3)_3N + C_3H_5{\cdot}OH,$$

and at the temperature at which the decomposition took place the allyl alcohol was decomposed, yielding acroleïn amongst other products. The action of heat on the chloride yielded a similar result, only traces of the mixed tertiary amine were formed.

Both in the case of the chloride and the hydroxide, the tertiary amine produced was almost entirely trimethylamine, the allyl radicle being almost entirely destroyed during the reaction.

The Action of Heat on the Chloride and Hydroxide of Tertiary Amyltrimethylammonium.

Trimethylamine in alcoholic solution was heated with chlorodimethylethylmethane; no combination, however, was found to occur, even after prolonged heating at 130°. The iodide was therefore substituted for the chloride. The iodide of amyltrimethylammonium which was produced was converted into the corresponding hydroxide with silver oxide, and the solution divided into two halves; one was directly subjected to the action of heat, the other was neutralised with hydrochloric acid and then decomposed also by heat.

In both cases the chief product of the decomposition was trimethylamine; only traces of the mixed amine was formed. In this respect the tertiary amyltrimethylammonium compounds differ from the isoamyl compounds obtained from trimethylamine and amyl iodide prepared from fusel oil. The trimethylamine produced by the decomposition of these compounds was identified by conversion into tetramethylammonium platinichloride.

The Action of Heat on the Chloride and Hydroxide of Trimethylphenylammonium.

The trimethylphenylammonium iodide was prepared from dimethylaniline and methyl iodide, and not directly from trimethylamine. An analysis was made of the salt. Iodine found = 48·2 per cent. Iodine in $(CH_3)_3(C_6H_5)NI$ = 48·3 per cent.

The chloride of trimethylphenylammonium is a deliquescent solid.

$$0{\cdot}1920 \text{ gram substance took } 9{\cdot}976\ \frac{10}{N}\ AgNO_3 = 18{\cdot}4 \text{ per cent. Cl.}$$

$$\text{Chlorine in } (CH_3)_3(C_6H_5)NCl = 18{\cdot}5 \text{ per cent.}$$

This salt, when subjected to the action of heat, decomposed quantitatively at a temperature much above 300° into methyl chloride and dimethylaniline, b. p. 190—192,

$$(CH_3)_3(C_6H_5)NCl = (CH_3)_2(C_6H_5)N + CH_3Cl,$$

while the hydroxide gave exactly similar results, only the mixed tertiary amine was formed,

$$(CH_3)_3(C_6H_5)N{\cdot}OH = (CH_3)_2(C_6H_5)N + CH_3{\cdot}OH.$$

The Action of Heat on the Chloride and Hydroxide of Trimethylbenzylammonium.

If benzyl chloride is added to a strong alcoholic solution of trimethylamine, the reaction is extremely energetic, and when the mixture cools crystals of trimethylbenzylammonium chloride separate from the solution. A small quantity was converted into the platinichloride and analysed.

0·5965 gram substance gave 0·1635 gram Pt = 27·41 per cent.
Pt in $[(CH_3)_3(C_7H_7)NCl]_2PtCl_4$ = 27·54 per cent.

The chloride, when heated to a temperature slightly above 300°, decomposes, yielding both gaseous and liquid products. The gas consisted chiefly of methyl chloride, but a liquid was also formed which collected in the U-tube used for condensing the tertiary amines.

After separation from the hydrochlorides of the amines, this liquid was found to boil at 175—177°, and from its properties and boiling point was benzyl chloride.

The hydrochlorides were evaporated almost to dryness, and treated with concentrated caustic soda solution; an oily layer at once separated which, on warming, yielded a considerable amount of trimethylamine, but there also remained behind a layer of the dimethylbenzylamine. This substance was extracted with ether, dried, and distilled. After one distillation it boiled between 178° and 179° (corrected).

On analysis—

0·2785 gram substance gave 24·0 c.c. nitrogen at 12° C. and 759 mm.

0·2885 gram substance gave 0·8450 gram CO_2 and 0·2545 gram H_2O.

	Calculated for $(CH_3)_2(C_7H_7)N$.	Found. I.	Found. II.
C.........	80·00	79·88	—
H.........	9·63	9·80	—
N.........	10·36	—	10·49

The decomposition of the chloride, when heated, is therefore largely into the mixed tertiary amines,

$$(CH_3)_3(C_7H_7)NCl = (CH_3)_2(C_7H_7)N + CH_3Cl.$$

The action of heat on the hydroxide does not yield nearly so much of the mixed tertiary amines; benzyl alcohol being produced in considerable quantities. The benzyl alcohol was identified by its boiling point and its easy conversion into benzoic acid by oxidation. The melting point of the acid was found to be 121·2°, and analysis of the silver salt gave 47·53 per cent. Ag (theoretical Ag in $C_6H_5{\cdot}COOAg$ = 47·16 per cent.). There was formed also during the reaction small quantities of a solid hydrocarbon which resembled diphenyl. That some of the mixed tertiary amine was amongst the products of decomposition was proved by a small quantity of an amine, b. p. 178—180°. This was mixed with methyl iodide, and an analysis made of the platinichloride. Platinum found = 27·7 per cent. Theoretical amount of platinum in $[(CH_3)_3(C_7H_7)NCl]_2PtCl_4$ = 27·5 per cent.

The chief mode of decomposition is therefore represented by the following equation:—

$$(CH_3)_3(C_7H_7)N{\cdot}OH = (CH_3)_3N + C_7H_7{\cdot}OH.$$

II. Mixed Quaternary Ammonium Compounds produced from Triethylamine.

The Action of Heat on the Chloride and Hydroxide of Triethylmethylammonium.

These compounds were prepared in the usual way from triethylamine and methyl iodide; and the action of heat on them gave substantially the same results as those obtained by Lossen (*Annalen*, **81**, pp. 376—383). The chief portion of the chloride was found to decompose into ethyl chloride and diethylmethylamine,

$$(C_2H_5)_3(CH_3)NCl = (C_2H_5)_2(CH_3)N + C_2H_5Cl.$$

The free tertiary amine was treated with methyl iodide, and after conversion into the chloroplatinate, on fractional precipitation with chloride of platinum, the following results were obtained:—

Fraction 1. 0·2368 gram salt gave 0·0753 gram Pt = 31·8 p. c.
Pt in $[(CH_3)_2(C_2H_5)_2NCl]_2PtCl_4$ = 31·8 „
Fraction 2. 0·251 gram salt gave 0·0778 gram Pt = 30·99 „
Fraction 3. 0·4172 gram salt gave 0·1303 gram Pt = 31·2 „
Pt in $[(CH_3)(C_2H_5)_3NCl]_2PtCl_4$ = 30·4 „

A certain quantity of the chloride must therefore decompose into chloride of methyl and triethylamine,

$$(CH_3)(C_2H_5)_3NCl = (C_2H_5)_3N + CH_3Cl.$$

The hydroxide, when heated, decomposes easily at a temperature not much above 100°, ethylene is produced, and the free tertiary amine consists *entirely* of the mixed amine,

$$(C_2H_5)_3(CH_3)N{\cdot}OH = (C_2H_5)_2(CH_3)N + C_2H_4 + H_2O.$$

The free base, when pure, boils at 66—67° (corrected). A combustion was made.

0·240 gram substance gave 0·604 gram CO_2 and 0·325 gram H_2O.

	Calculated for $(C_2H_5)_2(CH_3)N$.	Found.
C..............	68·96	68·64
H..............	14·94	15·05
N..............	16·09	—

The Action of Heat on the Chloride and Hydroxide of Dimethyldiethylammonium.

A considerable amount of the diethylmethylamine was treated with methyl iodide. The two substances united with the evolution of heat. Some of the iodide was analysed.

0·622 gram salt required 27·01 c.c. $\frac{N}{10}$ $AgNO_3$ solution = 55·4 p. c. I.
Iodine in $(C_2H_5)_2(CH_3)_2NI$ .... = 55·4 „

As Lossen had already heated the chloride and found a mixture of tertiary amines resulted, we did not repeat his experiment. The decomposition, however, of the hydroxide, although believed by him to take place as follows:—

$$(CH_3)_2(C_2H_5)_2N{\cdot}OH = (CH_3)_2(C_2H_5)N + C_2H_4 + H_2O,$$

had not been tried. This result was conjectured by Lossen from the results of Hofmann, who found that usually in a mixed quaternary ammonium hydroxide, the ethyl-group was first eliminated (as ethylene) when the compound was decomposed by heat. This conjecture of Lossen proved to be correct, for on heating the dimethyldiethylammonium hydroxide we obtained a tertiary amine which, when treated with methyl iodide, and converted into the platinum salt, gave the following numbers:—

0·302 gram salt gave 0·100 gram Pt........ = 33·1 per cent.
Pt in $[(CH_3)_3(C_2H_5)NCl]_2PtCl_4$ .... = 33·3 „

The ethylene was identified by absorbing it with bromine and taking the boiling point of the dibromethylene (b. p. 131·2°).

A curious point, however, was noticed with regard to the boiling point of the dimethylethylamine—it boiled completetely between 39° and 41°. Now, the dimethylethylamine obtained by the action of heat on trimethylethylammonium chloride boiled from 42° to 43° (p. 770). We have repeated the former experiment again with much larger quantities of salt, and with identically the same result; *the whole of the dimethylethylamine boils between* 39—41°. It has recently been suggested by Hantsch and Werner (*Ber.*, **23**, 11—30) that two isomers of the form NR′R′R″ are possible; whether we have here such substances we are unable to say at present, but propose to continue the investigation.

The Action of Heat on the Chloride and Hydroxide of Triethylbenzylammonium.

Triethylamine reacts at once with benzyl chloride when the two are mixed together. The chloride thus produced can be obtained in the crystalline form from a concentrated aqueous solution, but attempts to determine the water of crystallisation in it were unsuccessful, the salt decomposing when heated above 100°. The chloride was decomposed in the usual manner. Benzyl chloride was formed in considerable quantities and recognised by its smell and boiling point (178—7°). The free tertiary amines consisted almost entirely of triethylamine, only a very small quantity of the mixed amine being formed. The triethylamine was converted into tetrethylammonium iodide, and an iodine estimation made. Iodine found = 49·38 per cent. Iodine in $(C_2H_5)_4NI$ = 49·41 per cent. The less volatile base was mixed with ethyl iodide and converted into the platinichloride.

0·435 gram gave 0·1082 gram Pt	= 24·87 per cent.
Pt in $[(C_2H_5)_3(C_7H_7)NCl]_2PtCl_4$	= 24·62 „

The chief decomposition which the chloride therefore undergoes when heated is—

$$(C_2H_5)_3(C_7H_7)NCl = (C_2H_5)_3N + C_7H_7Cl.$$

This agrees with the decomposition of the iodide, for Bodewig has found (*Jahresbericht*, 1879, 435) that triethylbenzyl ammonium iodide when heated yields benzyl iodide and triethylamine. The hydroxide when heated seems to yield similar results; only traces of the mixed tertiary amine are produced. The benzyl alcohol was converted into benzoic acid and an analysis of the silver salt made (47·23 per cent. Ag found. Ag in $C_6H_5{\cdot}COOAg$ = 47·16 per cent.).

The decomposition of the base is chiefly as follows:—

$$(C_2H_5)_3(C_7H_7)N{\cdot}OH = (C_2H_5)_3N + C_7H_7{\cdot}OH.$$

An interesting point with regard to these triethylbenzylammonium compounds has been raised by Ladenburg (*Ber.*, **10**, 45); he holds that the iodide prepared by the action of diethylbenzylamine on ethyl iodide is not identical with that produced from the chloride obtained when triethylamine is allowed to react with benzyl chloride. We are at present engaged in preparing a number of these mixed quaternary ammonium compounds, and propose to study the properties of their salts, particularly the platinichlorides.

Conclusion.

From the forgoing results, it evidently seems to be a general rule that when a mixed quaternary ammonium chloride or hydroxide (made from trimethylamine or triethylamine) is heated, *a mixed tertiary amine is always produced.* The actual amount formed, however, varies very considerably with different compounds; for with the trimethylphenylammonium chloride the only product is dimethylphenylamine, whilst with the allyl- and isopropyl-trimethylammonium compounds, the chief tertiary amine formed by the action of heat is trimethylamine. If we take the chlorides, the *methyl-group* seems to be very easily eliminated from the molecule as *methyl chloride*, whilst in the case of the hydroxides the *ethyl-group* almost invariably splits away as ethylene. The reaction, therefore, seems to be more influenced by the nature of the decomposition products than by the introduced radicles; and we sometimes find that the chloride gives a much larger quantity of the mixed tertiary amine than the hydroxide:—

$$(CH_3)_3(C_7H_7)NCl = (CH_3)_2(C_7H_7)N + CH_3Cl,$$
$$(CH_3)_3(C_7H_7)N.OH = (CH_3)_3N + C_7H_7{\cdot}OH,$$

whilst in other cases we find the reverse to be the case:—

$$(C_2H_5)_3(CH_3)NCl = (C_2H_5)_3N + CH_3Cl,$$
$$(C_2H_5)_3(CH_3)N{\cdot}OH = (C_2H_5)_2(CH_3)N + C_2H_4 + H_2O.$$

Owing to the limited quantities of trimethylamine and triethylamine which we had to work with, the properties and boiling points of some of the mixed tertiary amines could not be determined; but as we propose to continue the research in somewhat the same direction with the view of studying the asymmetry of the nitrogen-atom, we may be able to fill up some of these gaps in a communication which we hope to bring before the Society at a future date.

University College,
London.

LIV.—*Note on a Compound from Benzoïn and Acetone.*

By **Francis R. Japp**, F.R.S., and **Julius Raschen**, Ph.D.

In a note in the Proceedings for May 20th, 1886, p. 203, "On Compounds from Benzil and Benzoïn with Alcohols," we described a compound melting at 249—250°, to which we assigned the formula $C_{46}H_{40}O_4$, believing it to be formed by the condensation of benzoïn with ethyl alcohol under the influence of caustic potash.

In the paper in the Transactions, in which an account of this result ought to have appeared, we mentioned (Trans., 1886, 833) that in the meantime we had found that this compound was not formed when pure alcohol was employed, and that its formation was due to some impurity contained in the methylated spirit which we had used instead of duty-paid alcohol. We reserved an account of the compound until we had ascertained the conditions of its formation.

We soon found that the impurity in question was acetone, and that the compound is apparently formed according to the equation

$$2C_{14}H_{12}O_2 + 2C_3H_6O + O = C_{34}H_{28}O_3 + 4H_2O.$$

The occurrence of an oxidation is assumed, partly because we found that a much better yield was obtained when air had access during the reaction, and partly because the formula $C_{34}H_{28}O_3$ agrees somewhat better with the results of analysis than the formula $C_{34}H_{30}O_3$, which would be that of a compound formed merely with elimination of water.

In order to prepare the compound, 10 grams of caustic potash were dissolved in a litre of alcohol; 40 grams of finely powdered benzoïn and 20 grams of acetone were added, and the whole was allowed to stand at ordinary temperatures in an open flask for several days, at first shaking the mixture from time to time, until the benzoïn had dissolved. The new compound gradually separated in very slender, silky needles. A quantity of potassium benzilate, formed by the joint action of air and caustic potash, could be readily removed by washing the product with water. The new compound was purified by recrystallisation from hot benzene, in which it is sparingly soluble, separating in slender needles on cooling. It was also recrystallised from boiling alcohol. It melted, as already stated, at 249—250°. The analyses agreed with the formula $C_{34}H_{28}O_3$.

	Substance.	CO_2.	H_2O.
I.	0·1327	0·4098	0·0731
II.	0·1399	0·4321	0·0784
III.	0·1409	0·4345	0·0780

	Calculated for $C_{34}H_{28}O_3$.		Found.		
			I.	II.	III.
C_{34}.....	408	84·30	84·22	84·23	84·12
H_{28}....	28	5·78	6·13	6·22	6·16
O_3.....	48	9·92	—	—	—
	484	100·00			

Analyses I and II were made with substance recrystallised from benzene; in III, the same specimen further recrystallised from alcohol was employed.

The formula $C_{34}H_{30}O_3$, on the other hand, would require C 83·95 and H 6·17 per cent.

The foregoing work was done in 1886, and its publication has been deferred, in the hope (hitherto unfulfilled) that an opportunity might be found of further investigating this compound. An attempt to prepare corresponding compounds from homologues of acetone gave no result under conditions similar to the foregoing.

In a paper in the July number of the Transactions (p. 644), Dr. A. Smith states that he has obtained from benzoïn and acetone by the action of potassium cyanide a compound, to which he assigns the formula $C_{24}H_{20}O_2$, deriving it from benzaldehyde and acetone, according to the equation—

$$3C_6H_5{\cdot}CHO + CH_3{\cdot}CO{\cdot}CH_3 = C_{24}H_{20}O_2 + 2H_2O.$$

No further details are given, so we are unable to say whether this compound is identical with that obtained by us. The formula $C_{24}H_{20}O_2$ requires C 84·71 and H 5·88, with which our analyses would also agree, although not so well as with the formula calculated by us.

Dr. Smith's promised investigation will doubtless decide as to the identity or non-identity of these compounds.

Normal School of Science,
South Kensington.

LV.—*Researches on Normal and Mixed Diazoamides.*

By RAPHAEL MELDOLA, F.R.S., and F. W. STREATFEILD, F.I.C.

AT the conclusion of our last communication on this subject (Trans., 1889, 442), it was stated that a new departure had been made by the discovery of a synthetical process for the production of mixed alkyl-diazoamides identical with those obtained by the direct alkylation of the mixed diazoamides. The three isomeric members of each series are, as we have frequently stated:—

I. Produced by the action of $X{\cdot}N_2{\cdot}Cl$ on $Y{\cdot}NHR'$.
II. Produced by the action of $Y{\cdot}N_2{\cdot}Cl$ on $X{\cdot}NHR'$.
III. Produced by the action of KOH and R′I on $X{\cdot}N_2H{\cdot}Y$.

It has been found that compounds I and II can in all cases be made to combine by simply boiling equal molecular proportions in alcoholic solution, the result of this combination being the isomeride No. III. The experiments are in the first place described in the order in which they were made.

I. SYNTHESIS OF MIXED ALKYL-DIAZOAMIDES.

1. Equal weights of the two compounds,

$(p)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$, (m. p. 187°) and
$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(p)$, (m. p. 174)

were dissolved in boiling alcohol and allowed to crystallise:—

After 1st crystallisation:	m. p.	150—154°
„ 2nd „	„	151—154°
„ 3rd „	„	151—154·5°
„ 4th „	„	151·5—156° (constant).

The product proved to be identical in appearance, melting point and other properties with that produced by the ethylation of parametadinitrodiazoamidobenzene (Trans., 1889, 418).

2. Equal weights of the two isomerides,

$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}Br(p)$, (m. p. 111°, Trans., 1889, 428) and
$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$, (m. p. 135—136°, Trans., 1889, 428)

were dissolved in alcohol and crystallised as before. After six crystallisations, the melting point was constant at 96—117°, and the product proved to be identical with that obtained by the ethylation of the mixed compound

$$(p)\mathrm{Br{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}NO_2}(m)$$

(Trans., 1889, 429).

3. Equal weights of the isomerides,

$(m)\mathrm{NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Br}(p)$, (m. p. 144°) and
$(p)\mathrm{Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}NO_2}(m)$, (m. p. 160·5—161°)

were dissolved in alcohol, and after two crystallisations gave a product melting at 125—138°, identical with that produced by the direct methylation of metanitroparabromodiazoamidobenzene (Trans., 1889, 427).

4. Equal weights of the isomerides,

$(p)\mathrm{CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Cl}(p)$, (m. p. 91—92°) and
$(p)\mathrm{Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}CH_3}(p)$, (m. p. 99·5—100°)

were dissolved in alcohol, and the solution kept boiling for two hours in a flask with a reflux condenser. The product consisted of flat plates, having a melting point of 79—81°, which after two more crystallisations became constant at 80—82°. This compound differs considerably in appearance from both of its constituents, and its identity with the product of the methylation of

$$(p)\mathrm{CH_3{\cdot}C_6H_4{\cdot}N_3H{\cdot}C_6H_4{\cdot}Cl}(p)$$

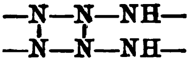
(Trans., 1889, 437) was shown not only by its crystalline form and melting point, but also by an examination of its products of decomposition by cold hydrochloric acid:

0·3123 gram in 10 c.c. of dilute acid (two parts strong acid to one of water) dissolved completely in 30 minutes, and gave on precipitation 0·3315 gram of azonaphthol. The latter proved to be a mixture of paratolueneazo-β-naphthol, and parachlorobenzeneazo-β-naphthol in approximately equal molecular proportions. The melting point of the mixed azonaphthols was 140—148°.

0·2490 gram gave 0·0814 gram AgCl = 8·08 per cent. Cl. Calculated for $\mathrm{Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + C_7H_7{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH}$: Cl = 6·52 per cent.

The foregoing results, which we have not thought it necessary to multiply by repetition with other pairs of isomerides, point to the conclusion that the mixed diazoamides and their alkyl-derivatives have double the molecular weight usually assigned to them, a conclusion which we have already made known in our last paper (Trans., 1889, 443), and which is in harmony with their behaviour on decomposition by acids, as well as by the various other reagents which have been tried upon them by previous investigators.

On considering the means by which two molecules of a diazoamide can unite, it appears most reasonable to assign the power of combination to the presence of unsaturated groups in the molecules. If the benzene rings have the ordinary constitution, and not that which exists in the diketone form of the ring, then the most unsaturated group present in these compounds is unquestionably the chain of nitrogen-atoms $\mathrm{—N{:}N\cdot NH—}$. Such groups might combine by the liberation of one bond of each of the two atoms of the N_2-group, $\mathrm{—N{:}N\cdot H—}$ becoming $—\ddot{\mathrm{N}}\cdot\ddot{\mathrm{N}}\cdot\mathrm{NH}—$. It seems not improbable that the association of the N_2-group with another nitrogen-atom would weaken the union between the atoms of that group. If two such chains of nitrogen-atoms combine, the result will be a four-atom ring of the form—



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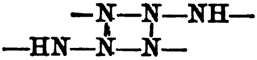
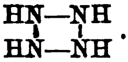
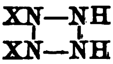


The mixed diazoamides may thus be regarded as derived from the hypothetical substance—



This compound may possibly be capable of isolation, and we propose to make experiments with the object of preparing it. The substance is the as yet unknown tetrimine, the di-derivatives of which are capable of two theoretical isomerides, viz., a consecutive and an opposite modification:—



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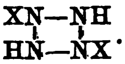
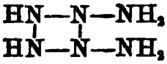


The mixed diazoamides might therefore be looked upon as derivatives of the diamidotetrimines:—



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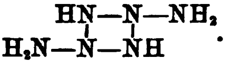
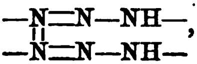
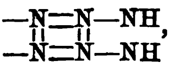


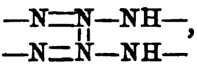
Another view respecting the combination of the nitrogen-atoms is that the coalescence occurs by the development of pentavalent functions on the part of one or more of the atoms. On this view we may have the groupings—



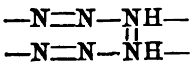
I.



II.



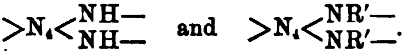
III.



IV.

It is impossible to decide between formula II and the one which we have previously suggested. The two formulæ are in fact identical in every respect, excepting the internal linking of the atoms of the nitrogen ring, and no advantage is gained by the use of the alternative formula. On the other hand formulæ I, III, and IV are open to the objection that they represent the nitrogen-atom as developing the pentavalent function for the purpose of combining with another atom of the same element, a view for which there is at present but little support.*

The force which binds together the two isomeric molecules constituting the mixed diazoamides is certainly of a more feeble character than that which is generally recognised at the present time as constituting true chemical combination. As will be seen further on from our experimental results, the compounds partake more or less of the character of the so-called "molecular compounds." Many chemists have, however, expressed the belief, in which we coincide, that there is no difference in the nature of the attraction which binds together the atoms in these "molecular compounds," and that which is concerned in ordinary stable combinations. The difference between the attractive forces in the two classes of combination is now very widely recognised as being one of degree and not of kind. Although this admission necessitates in many cases an extension of the ideas concerning variable valency, such as in double salts, the combination of salts with water of crystallisation, alcohol of crystallisation, &c., the particular compounds now under consideration admit of formulation on recognised principles on the view of their constitution previously expressed. But although the mode of combination suggested appears to us the most probable, we do not wish to insist upon the final adoption of the proposed formula. The outcome of our investigation at this stage has simply been to show that there is a residue of affinity between the two isomeric molecules, and that this residual attraction is most probably exerted between the pair of $-N{:}N\cdot NR'-$ groups. It seems legitimate to represent this combination by ordinary constitutional formulæ, but inasmuch as the mode of linkage between the nitrogen-atoms suggested by us raises the whole question of the constitution of molecular compounds, we shall throughout this paper, in all cases where possible, use formulæ representing only the fact of combination between the four nitrogen-atoms, without attempting to represent their precise mode of linkage. These formulæ will therefore contain the groups—



$$>N_4<\begin{matrix}NH-\\NH-\end{matrix} \quad \text{and} \quad >N_4<\begin{matrix}NR'-\\NR'-\end{matrix}.$$

---

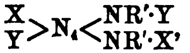
* The recent researches of Burch and Marsh (Trans., 1889, 656) may ultimately have some bearing on this point.

The discussion of the theoretical points arising from the kind of combination which our researches have revealed will be better undertaken when more light has been concentrated on the subject of molecular combination by independent lines of investigation.

II. COMBINATION AND ALKYLATION IN THE ABSENCE OF HYDROLYSING SOLVENTS.

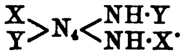
The foregoing syntheses having proved that the compound formed by direct alkylation could in all cases be prepared synthetically by combining the two isomerides $X\cdot N_2\cdot NR'\cdot Y$ and $Y\cdot N_2\cdot NR'\cdot X$, it naturally occurred to us whether the solvent (alcohol) is instrumental in bringing about the combination. In order to test this point, equal weights of the isomerides $(p)Cl\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot CH_3(p)$ and $(p)CH_3\cdot C_6H_4\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Cl(p)$ were boiled together in benzene solution, and the product crystallised out by the addition of petroleum. The compound thus obtained had a melting point of 80—82°, and was identical with that formed in alcoholic solution, thus proving that the combination is not dependent on the solvent. It was then found that combination could be also brought about by simply fusing the dry solids together in a test-tube immersed in boiling water.

The synthetical experiments thus show that mixed alkyl-diazoamides have the general formula—



$$\begin{matrix}X\\Y\end{matrix}>N_4<\begin{matrix}NR'\cdot Y\\NR'\cdot X\end{matrix},$$

and as they are produced by the direct alkylation of the mixed diazoamides, it follows that the latter must be constructed on a similar type:—



$$\begin{matrix}X\\Y\end{matrix}>N_4<\begin{matrix}NH\cdot Y\\NH\cdot X\end{matrix}.$$

We are aware that this result is at variance with that arrived at by other investigators. Thus Sarauw (*Ber.*, 1881, 2442, and 1882, 42), by acting on mixed diazoamides with phosgene in benzene solution, and decomposing the diazo-urea by heating with water, comes to the conclusion that the mixed diazoamides have the definite formula $X\cdot N_2\cdot NH\cdot Y$, in which Y is always the more negative radicle. A similar conclusion with respect to mixed diazoamides containing two dissimilar aromatic radicles has been arrived at by Goldschmidt and Molinari (*Ber.*, 1888, 2578), by a study of the action of phenyl isocyanate upon these compounds, and the decomposition of the diazo-urea thus formed. The results of both these investigators are, however, open to other interpretations, and the products obtained by them are of a very mixed character. We have no desire to offer any critical remarks upon these investigations at present, but with respect to the phenyl isocyanate reaction, we may point out that the quantity of this reagent used was based on the assumption that the mixed diazoamides had half the molecular weight which we believe them to possess, and that a selective action might very well take place under these circumstances. In other words, a fractional separation of the constituents of the molecule would account for the results obtained by Goldschmidt and Molinari. From our present standpoint, it appears desirable to reinvestigate the action of isocyanates upon the diazoamides, and we hope at some future period to make the necessary experiments.

It may fairly be urged that the mixed diazoamides have really the definite formula $X\cdot N_2\cdot NH\cdot Y$, and that duplication and molecular rearrangement with the formation of the two isomerides takes place during the alkylating process. In order to test this suggestion, a mixed diazoamide was prepared, and the dry silver salt alkylated in benzene. The following are the details of the experiment, in the carrying out of which we had the assistance of Mr. Frank Hughes, one of our students, to whom we wish to express our thanks for the valuable aid rendered in this as well as in other portions of the work:—

Parachloraniline was diazotised, and the solution of the diazochloride gradually poured into an alcoholic solution containing two molecular proportions of paratoluidine and some sodium acetate. The diazoamide was thrown out by dilution with water, and the product collected, washed with water, and twice crystallised from alcohol. It forms slender, yellow needles melting at 129—130° (Heumann and Oeconomides, *Ber.*, 1887, 909). The purity of the compound was established by analysis:—

0·1498 gram gave 0·0895 gram AgCl.

	Calculated for $C_7H_7\cdot N_2H\cdot C_6H_4\cdot Cl$.	Found.
Cl	14·46	14·78

In order to see whether the compound behaved as all mixed diazoamides and gave the usual mixture of four compounds, it was decomposed by hydrochloric acid by the method adopted by us throughout these investigations:—

0·2646 gram dissolved in 10 c.c. of strong acid in one hour without leaving any residue. The solution, on dilution with water and precipitation by adding to an alkaline solution of β-naphthol, gave a bright red precipitate, which, after being collected, washed with water, then with dilute acid, and again with water and dried, weighed 0·2950 gram = 111·4 per cent. The product was a mixture (m. p. 135—142°), and gave on analysis the following results:—

0·2716 gram gave 0·0700 gram AgCl:—

	Calculated for:— $\left\{\begin{matrix}\mathrm{C_7H_7\cdot N_2\cdot C_{10}H_6\cdot OH}\\ \mathrm{Cl\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH\cdot}\end{matrix}\right.$	Found.
Cl	6·52	6·37

The decomposition may therefore be considered as taking place quantitatively, in accordance with the equation—

$$\begin{matrix}(p)\mathrm{CH_3\cdot C_6H_4}\\ (p)\mathrm{Cl{-}C_6H_4}\end{matrix}\!>\!\mathrm{N_4}\!<\!\begin{matrix}\mathrm{NH\cdot C_6H_4\cdot Cl}(p)\\ \mathrm{NH\cdot C_6H_4\cdot CH_3}(p)\end{matrix} + 2\mathrm{HCl} = (p)\mathrm{CH_3\cdot C_6H_4\cdot N_2\cdot Cl}$$
$$+ (p)\mathrm{Cl\cdot C_6H_4\cdot N_2\cdot Cl} + (p)\mathrm{Cl\cdot C_6H_4\cdot NH_2} + (p)\mathrm{CH_3\cdot C_6H_4\cdot NH_2}.$$

This experiment is of importance as proving quantitatively that the unalkylated diazoamides decompose in precisely the same way as their alkyl-derivatives.

The silver salt was then prepared by dissolving the compound in alcohol with the addition of ammonia, and adding an excess of an ammoniacal solution of silver nitrate diluted with alcohol. The salt is precipitated at first as a yellow, gelatinous substance, which soon changes into a crystalline form, consisting of slender needles of a bright yellow colour. This property of first coming down gelatinous, and then becoming crystalline on standing, is characteristic of the silver salts of diazoamides (Trans., 1888, 671). The silver salt was collected, washed well with alcohol (in which it is quite insoluble), then with water, and finally with alcohol, and dried. The silver was determined by dissolving a known weight in strong nitric acid, diluting with water, and adding hydrochloric acid.

0·1804 gram gave 0·0735 gram AgCl.

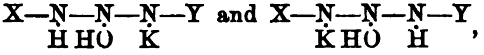
	Calculated for $\mathrm{(C_7H_7\cdot N_2Ag\cdot C_6H_4\cdot Cl)_2}$.	Found.
Ag	30·65	30·67

The silver salt does not readily react with methyl iodide when the latter is diluted with dry benzene. Six hours' cohobation with excess of methyl iodide mixed with benzene did not effect decomposition. The same mixture decomposed the silver salt only after being heated for three days in a sealed tube in a water-bath. Methyl iodide alone decomposed the salt when heated with the latter in a sealed tube in a water-bath for two hours. In both cases, after filtering off the silver iodide and allowing the solvent to evaporate, the same product was obtained, viz., the modification melting at 80—82°, identical with that obtained by alkylation with alcoholic potash and methyl iodide.

We admit that this experiment by itself does not prove that the mixed diazoamides have the formula which we have assigned to them, but it shows that the isomerides are not formed during the alkylation in the presence of water or alcohol, and thus pushes the explanation at least one stage further back, viz., to the period of the initial formation of the mixed unalkylated diazoamide. If then the latter, on the old view, have the formula $X{\cdot}N_2{\cdot}NH{\cdot}Y$, we must suppose that during alkylation two potassium salts are formed:

$$X{\cdot}N_2{\cdot}NK{\cdot}Y \text{ and } Y{\cdot}N_2{\cdot}NK{\cdot}X,$$

or, on the hydrolytic (electrolytic) theory (Goldschmidt and Meissler, *Ber.*, 1890, 253), that the intermediate compounds are produced:



$$X-\underset{H}{N}-\underset{HO}{N}-\underset{K}{N}-Y \text{ and } X-\underset{K}{N}-\underset{HO}{N}-\underset{H}{N}-Y,$$

these becoming alkylated and losing water and then combining. But these are arbitrary assumptions, and when we consider that the unalkylated compound decomposes in precisely the same way as the alkyl-derivative, it is, as it appears to us, more reasonable to conclude that the molecules are constructed on the same type, viz.:—

$$\begin{matrix}X\\Y\end{matrix}{>}N_4{<}\begin{matrix}NH{\cdot}Y\\NH{\cdot}X\end{matrix},\quad \begin{matrix}X\\Y\end{matrix}{>}N_4{<}\begin{matrix}NAg{\cdot}Y\\NAg{\cdot}X\end{matrix},\quad \begin{matrix}X\\Y\end{matrix}{>}N_4{<}\begin{matrix}N(CH_3){\cdot}Y\\N(CH_3){\cdot}X\end{matrix}.$$

III. SYNTHESIS OF HETEROGENEOUS MIXED ALKYL-DIAZOAMIDES.

The view that the combination of isomeric mixed diazoamides takes place by virtue of the unsaturated chain of nitrogen-atoms, leads naturally to the inference that other pairs of mixed diazoamides which are quite dissimilar should also be capable of forming compounds. That such is the case has already been made known in a preliminary note by one of us (Trans., 1889, 610). The field has thus been opened for the preparation of a class of compounds containing four dissimilar aromatic radicles and two similar or dissimilar alkyl-groups of the type:—

$$\begin{matrix}X\\A\end{matrix}{>}N_4{<}\begin{matrix}NR'{\cdot}Y\\NR'{\cdot}B\end{matrix}.$$

It is proposed to describe these as heterogeneous mixed diazoamides, to distinguish them from the former compounds, which contain only two different aromatic radicles, and which may be termed homogeneous mixed diazoamides. The latter might, of course, contain dissimilar alkyl radicles. When the compounds contain two similar aromatic radicles, they may be described as normal diazoamides (*Phil. Mag.*, 1887, 518).

A large number of synthetical experiments have been made with the object of ascertaining which pairs of alkyl-diazoamides could be combined. Our first attempt resulted in the successful synthesis of a very stable compound; but subsequent experiments gave less satisfactory results, the meaning of which did not become apparent until we had fully realised the fact that we were not dealing with ordinary cases of stable chemical combination. A general survey of the results thus far obtained enables us to state that every pair of mixed alkyl-diazoamides will combine, but the resulting compounds display various degrees of stability, according to the nature of the substituents in the aromatic radicles, and according to the alkyl radicle attached to the nitrogen-atom. A much larger number of syntheses will have to be studied before the precise conditions determining extreme stability can be determined, but it is obviously an investigation worthy of a large amount of labour. The class of compounds which we have had under investigation appears in fact of special interest from the point of view that it presents every degree of transition between stable chemical molecules and what would be called "molecular compounds." Thus homogeneous mixed alkyl-diazoamides, formed by the coalescence of two isomeric molecules, appear to be the most stable. The stability of heterogeneous mixed alkyl-diazoamides decreases as the aromatic nuclei become more acid by the introduction of acid substituents.

1. *Combination of Diazometanitrobenzene-methylparatoluide with Diazoparabromobenzene-methylparatoluide.*

The first of these compounds, which has not yet been described, was prepared by diazotising metanitraniline, and mixing the solution with the calculated quantity of methylparatoluidine oxalate dissolved in water containing an excess of sodium acetate. On mixing the solutions, a reddish precipitate at once forms, and this, after being collected and washed with cold water, was purified by two crystallisations from alcohol. The pure compound forms flat needles of an orange colour, and having a golden lustre. The melting point is 101—102°.

0·0920 gram gave 16·3 c.c. moist N at 19° C. and 763·3 mm. bar.

	Calculated for $NO_2{\cdot}C_6H_4{\cdot}N_3(CH_3){\cdot}C_7H_7$.	Found.
N	20·74	20·44

This compound and the other with which it had to be combined were weighed out in molecular proportions, dissolved in the smallest possible quantity of boiling alcohol, and the solution kept boiling for about an hour in a flask with a reflux condenser. On cooling, a crystalline deposit was obtained which, when dry, had a melting point of

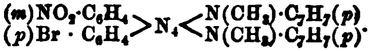
85—100°. The melting points of the constituents are 101—102° and 113—114°. After four crystallisations from alcohol, the melting point remained constant at 81—83°. A microscopic examination of the crystals at this stage showed that they consisted of a mixture of flat, yellow needles and ochreous plates, and we thought that no combination had taken place. The crystallisations from alcohol were therefore continued in the full expectation that one of the constituents would by this means be separated, and that the melting point would show a corresponding change. After eight crystallisations, however, the melting point was unchanged, and the substance still appeared to be a mixture of crystals under the microscope. If the product had been a mere mechanical mixture of the two components, it is impossible that continued fractional crystallisation should not remove a larger proportion of the more soluble constituent and thus, even if the melting point be disregarded as a criterion of individuality, the percentage of bromine must have been altered. After the eighth crystallisation, the following result was obtained on analysis:—

I. 0·1152 gram gave 0·0385 gram AgBr = 14·22 per cent. Br.

The substance was then crystallised once more from a large volume of alcohol, and the first crop of crystals filtered off as soon as they had separated. The melting point was unchanged, viz., 81—83°, and a bromine determination gave the following results:—

II. 0·1145 gram gave 0·0380 gram AgBr = 14·12 per cent. Br.

So far as melting point and analysis indicate chemical individuality, the compound was thus proved to be unresolvable by nine successive crystallisations from alcohol:—

	Calculated for  $\begin{matrix}(m)NO_2\cdot C_6H_4\\(p)Br\cdot C_6H_4\end{matrix}>N_4<\begin{matrix}N(CH_3)\cdot C_7H_7(p)\\N(CH_3)\cdot C_7H_7(p)\end{matrix}$.	Found. I.	 II.
Br	13·94	14·22	14·12

The possibility then occurred that the two constituents combined only in the hot solution, and that, on cooling, they separated out uncombined—in other words, that we were dealing with a case of unstable endothermic combination. We therefore took a considerable quantity of the substance which had been crystallised nine times, and which appeared under the microscope to consist of a mixture of crystals, and, after reducing it to an impalpable powder in an agate mortar, it was thrown into a large volume of cold alcohol, and allowed to stand with frequent agitation till about one-half of the whole quantity of substance had dissolved up. The solution was then filtered off, and the dissolved portion thrown out by dilution with water, after which it was collected and dried. The melting points of the two fractions when dry were—

I. Dissolved portion.	II. Residue.
81—86°	81—82°

The melting point of the dissolved portion was thus slightly altered, a fact which perhaps indicates an incipient separation of the constituents for reasons which will appear later on. The two fractions still had approximately the same chemical composition:—

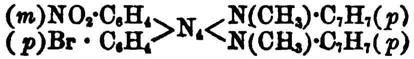
0·1070 gram (No. I) gave 0·0352 gram AgBr = 14·00 per cent. Br.
0·1406 „ (No. II) „ 0·0496 „ = 15·01 „

The constitution of the compound as deduced from the analytical results was in the next place verified by quantitative decomposition with hydrochloric acid:—

0·1784 gram (Nos. I and II mixed) dissolved immediately in 4·5 c.c. of strong acid without residue or coloration, and gave 0·1775 gram of azonaphthols, corresponding to 99·5 per cent. The crude azonaphthols had a melting point of 135—155°, and proved to be a mixture of metanitrobenzeneazo-β-naphthol and the corresponding parabromobenzene compound:—

0·1573 gram gave 0·0493 gram AgBr = 13·33 per cent. Br.

The mixture $NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH + Br{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH$ requires 12·9 per cent. Br. The decomposition is, therefore, quantitative in the sense of the equation:—



$$\begin{matrix}(m)NO_2{\cdot}C_6H_4\\(p)Br{\cdot}C_6H_4\end{matrix}>N_4<\begin{matrix}N(CH_3){\cdot}C_7H_7(p)\\N(CH_3){\cdot}C_7H_7(p)\end{matrix} + 2HCl = (m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl$$
$$+ (p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl + 2(p)C_7H_7{\cdot}NH{\cdot}CHl.$$

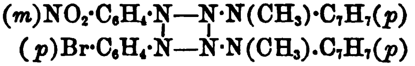
The percentage of azonaphthols calculated from the equation is:—

$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta)$	52·75
$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta)$	47·25

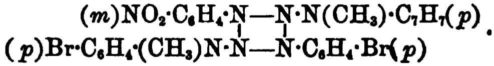
The bromine found corresponds to a mixture of the composition:—

$(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta)$	53·24
$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH(\beta)$	46·76

This synthesis, therefore, establishes the existence of heterogeneous mixed alkyl-diazoamides perfectly analogous to the corresponding homogeneous compounds. The occurrence of the two forms of crystals and the slight modification of melting point observed in the portion dissolved by cold alcohol point to the conclusion that the substance, although homogeneous in chemical composition, may consist of a mixture of isomerides. These may possibly be the two position-isomerides indicated by theory. It is evident that the two constituents may combine in two ways so as to give the consecutive and opposite modifications:—



$$\begin{array}{c}(m)NO_2{\cdot}C_6H_4{\cdot}N{-}N{\cdot}N(CH_3){\cdot}C_7H_7(p)\\ (p)Br{\cdot}C_6H_4{\cdot}N{-}N{\cdot}N(CH_3).C_7H_7(p)\end{array},$$



$$\begin{array}{c}(m)NO_2{\cdot}C_6H_4{\cdot}N{-}N{\cdot}N(CH_3){\cdot}C_7H_7(p)\\ (p)Br{\cdot}C_6H_4{\cdot}(CH_3)N{\cdot}N{-}N{\cdot}C_6H_4{\cdot}Br(p)\end{array}.$$

It is also possible that the two forms of crystals may really represent the components lying side by side, as in other ordinary cases of molecular combination. Whichever explanation may prove the correct one, the main fact established by this synthetical experiment is that combination of some kind takes place between the two constituents. The only other explanation of the results is that the two compounds have the same degree of solubility in alcohol, or, more exactly, that they dissolve in this solvent in the ratios of their molecular weights, so that, after the ten crystallisations given, the mixture still retained its equimolecular composition. In order to test this explanation, the following experiment was made:—

The two compounds which had been combined in the preceding experiment were weighed out in equimolecular proportions, and mixed intimately by grinding together to a fine powder in an agate mortar. The powder was then extracted by cold alcohol by allowing it to remain for two or three days under a considerable excess of the solvent, the action of the latter being promoted by occasional stirring. The residue was then collected on a filter and dried in the air, as it was found that the powder while wet with alcohol fused at once to an oil if placed in a water-oven, this fusion no doubt indicating the formation of the heterogeneous mixed alkyl-diazoamide described above. The air-dried residue was then analysed, two bromine estimations being made in each case, as the powder could be seen to consist of a mixture of the two constituents. The process of extraction, drying, and analysis was repeated as long as a sufficient residue was left for the bromine determinations. The following results were obtained:—

1. After the first extraction, the residue contained 13·44 per cent. of bromine (mean of two analyses).
2. After the second extraction, the residue contained 15·92 per cent. of bromine (mean of two analyses).
3. After the third extraction, the residue, which was only sufficient for one analysis, contained 23·32 per cent. of bromine.

The two compounds were thus shown to possess different degrees of solubility, the compound containing the parabromaniline residue being the less soluble. After three extractions with cold alcohol, the bromine found in the residue was only 3 per cent. below that required by the pure parabromo-compound. Comparing this with the 14 per cent. of bromine found after 10 crystallisations from hot alcohol, the existence of some combining power between the two compounds is clearly brought out.

2. *Combination of Diazo-β-naphthalene-methylparatoluide with Diazoparabromobenzene-methylparatoluide.*

The first of these compounds was prepared in the usual way by combining diazotised β-naphthylamine with the calculated quantity of methylparatoluidine emulsified in sodium acetate solution. The product, after crystallisation from alcohol, forms long, brownish needles melting sharply at 114°. The purity of the preparation was ascertained by analysis:—

0·1027 gram gave 13·4 c.c. moist N at 14° C. and 746·2 mm. bar.

	Calculated for $C_{10}H_7{\cdot}N_2{\cdot}N(CH_3){\cdot}C_7H_7$.	Found.
N	15·27	15·25

This and the parabromo-compound were weighed out in molecular proportions and boiled in alcoholic solution for 2—3 hours. The product was collected and crystallised from alcohol in order to ascertain whether a compound of definite composition and melting point could be obtained. The two compounds have practically the same melting point (114°). The results of five crystallisations were 87—88°, 87—89°, 87·5—90°, 88—90°, 88·5—90°. It was evident from the melting points that combination had also occurred in this case. The product was analysed at this stage with the following results:—

0·1054 gram gave 13·6 c.c. moist N at 15° C. and 746·5 mm. bar.
0·2265 „ „ 0·0781 gram AgBr.

	Calculated for $\substack{C_{10}H_7\\ Br{\cdot}C_6H_4}>N_4<\substack{N(CH_3){\cdot}C_7H_7\\ N(CH_3){\cdot}C_7H_7}$	Found.
N	14·51	14·81
Br	13·92	14 67

After a sixth crystallisation, the melting point was 88—90°:—

0·1704 gram gave 0·0580 gram AgBr = 14·48 p. c. Br.

After a seventh crystallisation, the substance was examined microscopically, and seen to consist of a mixture of brownish needles and ill-defined, ochreous scales. The crystals were separated as far as possible in order to determine the melting point:—Ochreous scales, 87—88°; brown needles, 87—89°. After an eighth crystallisation of the total product, the melting point was 87—88°.

0·1835 gram gave 0·0630 gram AgBr = 14·61 p. c. Br.

After a tenth crystallisation, the same mixture of crystals was observed: needles, m. p. 86·5—89°; scales, m. p. 86·5—87·5°.

0·1557 gram gave 0·0492 gram AgBr = 13·44 p. c. Br.

This experiment, as far as it goes, fully supports the result of the previous synthesis. The heterogeneous compound thus obtained could not, however, be decomposed quantitatively by our usual method, because of the presence of the β-naphthalene residue, which complicates the results of decomposition by acid, owing to the formation of an amidoazo-compound, no doubt $Br\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot NH_2(\beta)$. That actual combination had occurred, and that we were not dealing with a mere mixture of compounds soluble in alcohol in the ratios of their molecular weights, was established by the following control experiment:—

The two compounds were weighed out in equimolecular proportions, and reduced to an impalpable powder by grinding together in an agate mortar. The mixture was extracted four times in succession with cold alcohol, and the dry residue analysed after each extraction with the following results:—

I. 0·1644 gram gave 0·0529 gram AgBr = 13·69 p. c. Br.
II. 0·2203 „ „ 0·0604 „ „ = 11·66 „
III. 0·1618 „ „ 0·0329 „ „ = 8·65 „
IV. 0·2345 „ „ 0·0307 „ „ = 5·57 „

The substance was all used up by the last analysis, but the result is conclusive as proving the unequal solubilities of the two compounds. It is of interest to note that the order of solubility is the reverse of that observed in the preceding synthesis, *i.e.*, the parabromo-compound is the more soluble.

3. *Other Syntheses and General Remarks on the Nature of the Combination between Mixed Alkyl-diazoamides.*

Several other syntheses, in addition to the foregoing, have been studied, but it will be only necessary to give an abstract of the results and the conclusions to which they have led:—

A. The pair of compounds $(\beta)C_{10}H_7\cdot N_2\cdot N(CH_3)\cdot C_7H_7(p)$ (m. p. 114°) and $(p)C_7H_7\cdot N_2\cdot N(CH_3)\cdot C_6H_4\cdot Br(p)$ (m. p. 99·5°) combined with the formation of a compound having a most indefinite range of melting points. After 10 crystallisations, the product melted at 110—113°, and we thought that the β-naphthalene compound was simply being removed as the less soluble constituent. Analysis showed, however, that this was not the case, as the product contained 16·45 per cent. of bromine.

B. The pair $(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_7H_7(p)$ (m. p. 101—102°) and $(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$ (m. p. 135—136°) gave a product having a very vague melting point. Commencing at 104—113°, after six crystallisations, the melting point was 135—136°, and analysis showed that the parabromo-compound had been separated out in an unaltered condition. The combination in this case was of an extremely feeble character.

C. The pair $(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_7H_7(p)$ (m. p. 101—102°) and $(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}Br(p)$ (m. p. 111°) gave a product melting at about 83—97°. The melting point continued to rise and the percentage of bromine to increase after each crystallisation. After 12 crystallisations, the pure metanitroparabromo-compound (m. p. 111°) was separated out, so that in this case also the combination was of a very feeble kind.

D. The pair $(m)NO_2.C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_7H_7(p)$ (m. p. 101—102°) and $(p)C_7H_7{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Cl(p)$ (m. p. 92°) gave a product melting at 75—85°. After 11 crystallisations, the melting point was about 102°, and the product was free from chlorine, so that the metanitro-compound had been separated out.

E. The pair $(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_7H_7(p)$ (m. p. 101—102°) and $(p)C_7H_7{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Br(p)$ (m. p. 99·5°) gave a product melting at 70—72°. After six crystallisations, the metanitro-compound was separated. The experiment was repeated by dissolving the two compounds in a minimum quantity of hot alcohol, and then sealing up the solution in a tube which was heated in a water-bath for 4—5 hours. The product was the same as before, and after six crystallisations the pure metanitro-compound was separated out. From this experiment, it appears that heating in a sealed tube under pressure does not promote combination between two dissimilar alkyl-diazoamides which possess only a feeble power of combining.

The general tendency of these synthetical experiments is to show that when the two alkyl-diazoamides are very dissimilar, and especially when they contain radicles made acid by NO_2, Br, or Cl, the combination is of the feeblest character, and the heterogeneous compound is easily resolvable by crystallisation from alcohol. The lowering of melting point at first observed in the products of all the experiments indicates, however, that some kind of combination does occur. This fact is analogous to that so frequently observed in the course of the present researches, viz., that the melting points of the homogeneous mixed compounds, whether formed by direct alkylation or by the coalescence of the isomerides, are invariably lower than that of either of the constituents (Trans., 1889, 431). In other words, $X\cdot N_2\cdot NR'\cdot Y$ and $Y\cdot N_2\cdot NR'\cdot X$ combine to give a product of lower melting point than either isomeride, this product being possessed of the highest degree of stability. On the other hand, $X\cdot N_2\cdot NR'\cdot Y$ and $A\cdot N_2\cdot NR'\cdot B$ combine to give a product of lower melting point than either of the constituents, but possessed of a lower degree of stability, and more or less easily resolvable, according to the acidity or degree of dissimilarity of the constituents.

The heterogeneous mixed compounds, as a class, are decidedly less stable, *i e.*, they partake more distinctly of the characters of molecular compounds than the homogeneous mixed alkyl-diazoamides. The most stable that we have hitherto succeeded in preparing, viz., the two described at the beginning of this section, although stable up to the number of crystallisations described in the experiments, may ultimately be resolved by continued fractional crystallisation, but the separation, when once combination has been effected by heating the solution, is far more difficult than when the finely-powdered constituents are extracted with the cold solvent, as appears from the experiments previously recorded. It must be pointed out, however, that the two heterogeneous compounds referred to are, strictly speaking, partly homogeneous, as both pairs contain the same group, $N(CH_3)\cdot C_7H_7$, and they are heterogeneous in so far as they contain the radicles $(m)NO_2\cdot C_6H_4$, $(\beta)C_{10}H_7$, and $(p)Br\cdot C_6H_4$. The most stable combination would no doubt occur between pairs containing no acid substituents, but the practical difficulties in the way of investigating such pairs are insuperable, as we have already pointed out (Trans., 1888, 665, and 1889, 413). The alkyl-derivatives of mixed diazoamides, obtained from unsubstituted bases such as aniline and homologues, &c., are oily at ordinary temperatures, and in the next place it is essential that at least one of the pair should contain a halogen-atom, as by this means alone can the fact and degree of combination be satisfactorily ascertained by analysis. Our general experience in effecting combination between dissimilar alkyl-diazoamides goes to show that the most favourable conditions for securing the result are rapid crystallisation from the hot concentrated solution. We have found it best to place the beaker containing the hot alcoholic solution in cold water, and to stir the liquid with a glass rod till it is quite cold and the separation of the crystalline deposit is complete.

There is one consideration arising from our experiments which is of importance, both in connection with the general question of the constitution of the mixed diazoamides, and also as explaining many observations with reference to these compounds which have hitherto been enigmatical. According to the conclusion at which we have arrived, these compounds are formed by the coalescence of the isomerides $X{\cdot}N_2{\cdot}NH{\cdot}Y$ and $Y{\cdot}N_2{\cdot}NH{\cdot}X$, and possess the formula :—

$$\begin{matrix}X\\Y\end{matrix}{>}N_4{<}\begin{matrix}NH{\cdot}Y\\NH{\cdot}X\end{matrix}.$$

Now, it has been shown above that when all the radicles of a heterogeneous mixed diazoamide contain acid substituents, the combination between the constituent pair is of the feeblest kind. It thus seemed not improbable that mixed compounds containing only isomerides, and not dissimilar constituents, should be less stable when containing acid radicles than when free from such substituents. By continued crystallisation, therefore, it seemed likely that such homogeneous mixed compounds might be split up into the two isomerides. One experiment which we have carried out certainly supports this view. In our last paper we described the compound obtained by the action of diazotised metanitraniline on parabromaniline and the methylation of the product (Trans., 1889, 427). As the melting point of this compound was vague (125—137·5°), and it contained NO_2 and Br in the radicles, it seemed a promising compound for our purpose. The purity of the preparation, from a chemical point of view, had previously been proved by analysis (*loc. cit.*). This substance was crystallised repeatedly from alcohol, and it was found that the melting point rose after each crystallisation, becoming constant after 10 crystallisations at 160—161°. The chemical composition was unchanged, and it was evident that we had separated out the compound $(p)Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}NO_2(m)$, *i.e.*, the compound produced by the action of diazotised parabromaniline on methylmeta-, nitraniline (Trans., 1889, 426). A parallel experiment was made with the synthetical product obtained by combining the two isomerides,

$$(p)\ Br{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}NO_2(m) \text{ and}$$
$$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Br(p),$$

described in the first part of the present paper (Experiment 3, Section I). After 10 crystallisations, the first of these (m. p. 160—161°) was separated out as before.

The foregoing observation enables us to explain a result which for more than two years has been standing in our note-book as awaiting further elucidation. In a former paper we described the two isomerides,

$(m)NO_2{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}Cl(p)$...... m. p. 106°,
$(p)Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}N(C_2H_5){\cdot}C_6H_4{\cdot}NO_2(m)$...... m. p. 129 5°,

stating at the time that the third member of the triplet was wanting, owing to the difficulty of getting diazotised metanitraniline to combine with parachloraniline or *vice versâ* (Trans., 1888, 675). It is now evident that the difficulty of preparing mixed diazoamides from the nitranilines and parachloraniline is due to the extremely acid substituents.

Before we had realised the true nature of these mixed diazoamides, an attempt had been made to complete this triplet in the usual way. Diazotised metanitraniline was combined with parachloraniline suspended in sodium acetate solution, and the product crystallised from alcohol. After three crystallisations, the compound formed small, yellow needles melting at 143—143·5°. As we were not at that time concerned with the mixed diazoamides so much as with their alkyl-derivatives, the whole product was ethylated in order to see whether the third ethyl-derivative could be obtained. The melting point of the ethyl-derivative was vague at first, viz., 113—114°, 113·5—115·5°, 113·5—122·5°, 126—126·5°. After six crystallisations, the melting point was 129—129·5°, and analysis gave the following results:—

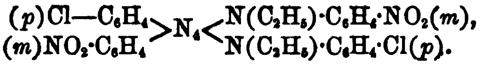
0·0832 gram gave 12·9 c.c. moist N at 12·5° C. and 749·9 mm. bar.
0·1565 „ „ 0·0743 gram AgCl.

	Calculated for $NO_2 \cdot C_6H_4 \cdot N_3(C_2H_5) \cdot C_6H_4 \cdot Cl$.	Found.
N	18·38	18·09
Cl	11·65	11·74

We concluded, therefore, either that the third member of the triplet had the same melting point as one of the isomerides, or that this pair of amines formed an exception to the rule of what we then called "triple isomerism." Another experiment was then made by reversing the order of combination. Parachloraniline was diazotised and added to the calculated quantity of metanitraniline dissolved in cold alcohol mixed with sodium acetate solution. The product was collected, washed, and ethylated as before; the ethyl-derivative again showed a vagueness of melting point, viz., 89—94°, 92—111°, 118—124°, 126—128·5°. After eight crystallisations, the melting point was constant at 129·5°, and it was evident that we had separated out the same product as before. This product was then compared with $(p)Cl \cdot C_6H_4 \cdot N_2 \cdot N(C_2H_5) \cdot C_6H_4 \cdot NO_2(m)$, with which it appeared to be identical, by the method of quantitative decomposition:—

0·2634 gram dissolved in 10 c.c. of strong HCl in three hours, leaving a residue of 0·0144 gram. The azonaphthol weighed 0·2350 gram, and proved to be parachlorobenzeneazo-β-naphthol (m. p.

161—163°), and not a mixture, thus proving the identity of the product with that obtained by the action of diazotised parachloraniline or ethylmetanitraniline. From the position to which our researches have brought us, we are now enabled to state that this result is not opposed to the rule of "triple isomerism." The mixed alkyl-diazoamide is no doubt formed in this as in all other cases, viz., the compound:—

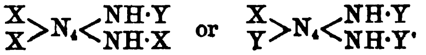


$$\begin{array}{l}(p)\mathrm{Cl}-C_6H_4\\(m)NO_2\cdot C_6H_4\end{array}>N_4<\begin{array}{l}N(C_2H_5)\cdot C_6H_4\cdot NO_2(m),\\N(C_2H_5)\cdot C_6H_4\cdot \mathrm{Cl}(p).\end{array}$$

But this, owing to the acid character of the substituents, belongs to the less stable forms of mixed alkyl-diazoamides, and is therefore resolved by continued crystallisation, the gradual rise in melting point simply indicating the gradual removal of the less soluble $(m)NO_2\cdot C_6H_4\cdot N_2\cdot N(C_2H_5)\cdot C_6H_4\cdot \mathrm{Cl}(p)$.

The outcome of these experiments is to show that the mixed alkyl-diazoamides and the unalkylated compounds from which they are derived have in all probability the double formula which we have proposed. If no acid substituents are present, the stability of the molecule is such that it is unresolvable by any ordinary number of crystallisations, and the compound would pass for a chemical individual in the ordinary acceptation of the term. As the molecule becomes more acid, the combination of the pair of isomerides is weakened, and separation can be effected, as seen by the above results. When the constituent pairs are quite dissimilar and both contain acid radicles, the combination assumes that form which would be called "molecular," as in the case of the heterogeneous mixed compounds, which can be separated with comparative readiness. There is, as we have previously stated, a distinct series of steps connecting what is in all respects ordinary chemical combination with "molecular" combination.

Many considerations and new lines of investigation are suggested by these conclusions. Thus, it is possible that previous investigators dealing with these compounds may, by repeated crystallisation, have obtained products of the simple type $X\cdot N_2\cdot NH\cdot Y$, or mixtures of the latter with the compounds of the double type. By working with mixed unalkylated compounds containing acid substituents, it is possible that the separation of the isomerides $X\cdot N_2\cdot NH\cdot Y$ and $Y\cdot N_2\cdot NH\cdot X$ may be effected, as we have already succeeded in doing with the alkyl-derivatives. Experiments in this direction will be undertaken, and the results made known to the Society in a future communication. We may also take the present opportunity of pointing out that the difficulty of obtaining mixed diazoamides in a state of purity (Trans., 1889, 413) is probably due to an actual combination between a portion of the mixed compound and a small quantity of the normal compound which may be formed at the same time. Such combination would be most likely to occur at the time of formation. Thus, supposing $X{\cdot}N_2{\cdot}Cl$ to act upon $Y{\cdot}NH_2$, the two compounds $X{\cdot}N_2{\cdot}NH{\cdot}Y$ and $Y{\cdot}N_2{\cdot}NH{\cdot}X$ are the chief products, and these combine to form the mixed diazoamide. If at the same time a trace of the normal compound $X{\cdot}N_2{\cdot}NH{\cdot}X$ or $Y{\cdot}N_2{\cdot}NH{\cdot}Y$ is also formed, this might be taken up by one or both of the isomerides with the formation of traces of the intermediate products



$$\begin{matrix}X\\X\end{matrix}>N_4<\begin{matrix}NH{\cdot}Y\\NH{\cdot}X\end{matrix} \quad \text{or} \quad \begin{matrix}X\\Y\end{matrix}>N_4<\begin{matrix}NH{\cdot}Y\\NH{\cdot}Y\end{matrix}.$$

A small proportion of such a compound would be inseparable from the mixed diazoamide, and would raise or lower the percentage of halogen in compounds containing these substituents. The way is thus indicated for the synthesis of compounds containing partly normal and partly mixed diazoamides.

IV. DETERMINATION OF MOLECULAR WEIGHTS BY RAOULT'S METHOD.

In order to ascertain whether the mixed alkyl-diazoamides gave evidence of the double molecular weight to which the chemical results so distinctly pointed, the depression of freezing point was observed in a carefully purified triplet of isomerides dissolved in pure benzene, specially prepared for this purpose by Messrs. Read Holliday and Sons. The results are given below, the usual symbols being adopted, viz.:—

E, observed setting point of the solution.
C, depression of freezing point.
A, coefficient of depression (depression produced by 1 gram of substance in 100 grams of solvent).
M, molecular weight calculated from foregoing values.

1. $(p)CH_3{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3){\cdot}C_6H_4{\cdot}Cl(p)$...... m. p. 92°.

Setting point of benzene, 5·3°. Weight of solvent, 38·55 grams. Weight of substance, 0·3876 gram. Mol. wt., 259·5.

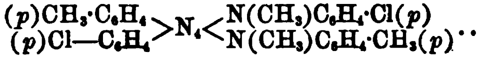
E.	C.	A.	M.
5·1	0·2	0·199	246
5·1	0·2	0·199	246

0·3439 gram substance added; total weight in solution, 0·7315 gram.

4·9	0·4	0·211	232
4·9	0·4	0·211	232

0·3781 gram substance added; total weight in solution, 1·1096 grams.

E.	C.	A.	M.
4·75	0·55	0·191	256
4·75	0·55	0·191	256

2. 

$$\begin{matrix}(p)CH_3{\cdot}C_6H_4 \\ (p)Cl{-}C_6H_4\end{matrix}{>}N_4{<}\begin{matrix}N(CH_3)C_6H_4{\cdot}Cl(p) \\ N(CH_3)C_6H_4{\cdot}CH_3(p)\end{matrix}\ldots \left\{\begin{matrix}\text{m. p. } 81\text{—}83^\circ. \\ \text{Mol. wt. } 519.\end{matrix}\right.$$

Setting point of benzene, 5·3°. Weight of solvent, 66·14 grams. Weight of substance, 0·3607 gram.

E.	C.	A.	M.
5·2	0·1	0·183	267
5·2	0·1	0·183	267

0·7114 gram substance added; total weight in solution, 1·0721 gram.

5·1	0·2	0·163	300

1·1558 gram substance added; total weight in solution, 2·2279 grams.

4·95	0·35	0·184	266
4·95	0·35	0·184	266

3. $(p)Cl{\cdot}C_6H_4{\cdot}N_2{\cdot}N(CH_3)C_6H_4{\cdot}CH_3(p)$..... m. p. 98·5—99·5°.

Setting point of benzene, 5·3°. Weight of solvent, 66·29 grams. Weight of substance, 0·3460 gram.

E.	C.	A.	M.
5·2	0·10	0·191	256·5
5·2	0·10	0·191	256·5

0·3573 gram substance added; total weight in solution, 0·7033 gram.

5·12	0·18	0·169	290
5·12	0·18	0·169	290

0·3489 gram substance added; total weight in solution, 1·0522 grams.

5·0	0·30	0·189	259·2
5·0	0·30	0·189	259·2

The mean results for the three isomerides are:—

1.	2.	3.	Calculated.
244·6	277·6	268·5	259·5

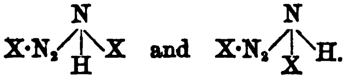
The method of Raoult in this case, therefore, gives no intimation of the fact that compound No. 2 has double the molecular weight of Nos. 1 and 3, a fact from which there is no escape in view of the circumstance that compound No. 2 can be synthesised by boiling equal weights of Nos. 1 and 3 in any suitable solvent.

This result is not altogether surprising when it is borne in mind that the combination between the isomerides 1 and 3 is more or less of the nature of molecular combination. Since Raoult's method is still on its trial, and the limits of its applicability are as yet without rigid definition, we have thought it desirable to place these results upon record, although they are negative so far as concerns our present investigation (see *Chem. News*, **60**, 66). Other cases of molecular compounds giving abnormal results are already known. Thus, Anschütz (*Ann. Chem. Pharm.*, **253**, 343) found that naphthalene picrate in benzene gave results indicating decomposition into naphthalene and picric acid. It is quite possible that the molecule of the mixed diazoamides may similarly undergo dissociation in solution.

Still more striking, because of the remarkable parallelism with our compounds, are Anschütz's results with the tartaric acids. This investigator found that the methyl ethers of dextro- and lævotartaric acid combined either in hot or cold solution to form the methyl ether of racemic acid. The free acids also combine under similar circumstances to form racemic acid, and the latter, by means of the sodium-ammonium salt, can be again resolved into the two tartaric acids. From this it is concluded that the inactive racemic acid is formed by the coalescence of the two active acids, and not that each of the active acids undergoes transformation into racemic acid. Similar reasoning points to the conclusion that the ether of the latter acid is composed of equal molecules of the two tartaric acid ethers. Although from this evidence it follows that racemic acid and ether have double the molecular weight of tartaric acid and ether, the vapour-density of racemic ether is the same as that of the tartaric ethers, viz., one-half that required by the double formula, a fact which is explained by the dissociation of the racemic ether into its constituents at the temperature of vaporisation (*Ber.*, 1885, 1397). In like manner, Anschütz has found that the dimethyl ethers of diacetyldextro- and diacetyllævo-tartaric acids combine to form the dimethyl ether of diacetylracemic acid. This last compound must therefore have double the molecular weight of its constituents. Nevertheless, Raoult's method gives results indicating half this molecular weight (*Ber.*, 1889, 980).

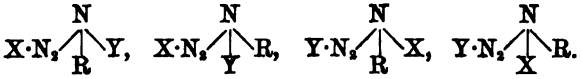
Theoretical Considerations.

During the course of these investigations, which were commenced more than four years ago, the stereochemical hypothesis of Le Bel and Van't Hoff has been developed in various directions, and has found many supporters, especially in Germany, where it has been applied with more or less success to the elucidation of certain cases of isomerism. We have never lost sight of the possibility of explaining the existence of three isomeric alkyl-diazoamides as a case of stereochemical isomerism, but our considerations have thus far convinced us that this hypothesis is inadequate in its present condition to account satisfactorily for the facts brought to light by our experiments. The nitrogen-atom may be regarded in its pentavalent form as occupying the centre of a double tetrahedron, so that three of its bonds are in one plane and the two other bonds in a different plane (Willgerodt, *Journ. prakt. Chem.* [2], **37**, 449). This idea has been taken up recently by Burch and Marsh (Trans., 1889, 656. See also Behrend, *Ber.*, 1890, 454), who have shown that in certain amines the nitrogen-atom is to some extent possessed of a residue of affinity which leads two molecules to combine. Hantzsch and Werner (*Ber.*, 1890, 11) have also attempted to develop the hypothesis that the bonds of the trivalent nitrogen-atom are directed along the edges of a regular tetrahedron, which amounts to the supposition that two of the bonds are in one plane and the third in a different plane. Before the appearance of the paper referred to, we had attempted to apply this view to the diazoamides, but had abandoned it as insufficient. Thus, to take the simplest possible case, every diazoamide should on this hypothesis be capable of existing in the two forms—



$$\mathrm{X{\cdot}N_2}\overset{\mathrm{N}}{\underset{\mathrm{H}}{\diagup|\diagdown}}\mathrm{X}\quad\text{and}\quad\mathrm{X{\cdot}N_2}\overset{\mathrm{N}}{\underset{\mathrm{X}}{\diagup|\diagdown}}\mathrm{H}.$$

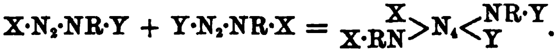
There is at present no evidence for the existence of such isomerism. Every mixed diazoamide or alkyl-diazoamide should similarly be capable of the quadruple isomerism—



$$\mathrm{X{\cdot}N_2}\overset{\mathrm{N}}{\underset{\mathrm{R}}{\diagup|\diagdown}}\mathrm{Y},\quad\mathrm{X{\cdot}N_2}\overset{\mathrm{N}}{\underset{\mathrm{Y}}{\diagup|\diagdown}}\mathrm{R},\quad\mathrm{Y{\cdot}N_2}\overset{\mathrm{N}}{\underset{\mathrm{R}}{\diagup|\diagdown}}\mathrm{X},\quad\mathrm{Y{\cdot}N_2}\overset{\mathrm{N}}{\underset{\mathrm{X}}{\diagup|\diagdown}}\mathrm{R}.$$

We have not the slightest evidence, however, that the compound produced by the action of $\mathrm{X{\cdot}N_2{\cdot}Cl}$ on $\mathrm{Y{\cdot}NHR}$ is susceptible of two geometrical isomerides. On the other hand, the triple isomerism described by us is shown not only by difference in melting point, but by difference on decomposition by acid. The alkyl-derivative of a mixed diazoamide and the unalkylated compound decompose quantitatively as though both isomerides, $X{\cdot}N_2{\cdot}NH{\cdot}Y$ and $Y{\cdot}N_2{\cdot}NH{\cdot}X$, were present, and when an alkyl radicle is introduced the latter remains attached to both X and Y after decomposition. These facts are in no way explained by the stereochemical hypothesis, and we have not thought it necessary to invoke its aid. Our results lead us to believe that the simplest explanation is that in the mixed diazoamides the molecule undergoes polymerisation.

The main point now demanding explanation is why diazoamides of the form $X{\cdot}N_2{\cdot}NH{\cdot}X$, $X{\cdot}N_2{\cdot}NR{\cdot}X$, $X{\cdot}N_2{\cdot}NR{\cdot}Y$, and $Y{\cdot}N_2{\cdot}NR{\cdot}X$ should be in a condition of sufficient internal equilibrium for the molecules to exist in that form without polymerisation. It is possible that the first two are sufficiently symmetrical, but the two latter, being unsymmetrical, are in a condition of unstable equilibrium, and combine (as experiment has shown to be the case) in order to form a more symmetrical molecule—



$$X{\cdot}N_2{\cdot}NR{\cdot}Y + Y{\cdot}N_2{\cdot}NR{\cdot}X = {}_{X\cdot RN}^{\;\;\;\;X}\!\!>N_4<\!{}_{Y}^{NR\cdot Y}.$$

The present research has been carried on with the aid of a grant from the Research Fund of the Society.

Finsbury Technical College.

LVI.—*Note on the Action of Nitric Acid on Dibrom-α-naphthol.*

By Raphael Meldola, F.R.S., and Frank Hughes.

In a former paper (this vol., 393), we described the product, monobromindone, which is formed by the action of fuming nitric acid on dibrom-α-naphthol. In the same paper, we stated that the products varied according to the strength of the nitric acid, the ordinary 1·42 sp. gr. acid giving an additive compound which appears to furnish a mixture of dinitronaphthol and nitrobromonaphthol. The investigation of this additive product will be resumed, as it may help to throw light on the mechanism of substitution in aromatic compounds. In continuing our experiments, we have found that if the nitric acid is not fully up to the strength of 1·5 sp. gr., the bromindone is mixed with some other product which we have not been able to separate in a state of purity, but which has been proved to be monobrom-α-naphthaquinone. We may state, also, that if the nitric acid is below 1·5 sp. gr., the yield of γ-naphthaquinone is much diminished.*

Experiments have also been made to see whether the supposed peribrom-α-naphthol, which we suggested to be the source of the quinone (this vol., 634), could be separated from the dibrom-α-naphthol by crystallisation. These experiments have hitherto been unsuccessful, but they have incidentally enabled us to ascertain the actual yield of the quinone. Thus a quantity of pure dibrom-α-naphthol was dissolved in petroleum and allowed to crystallise. The mother liquor, on evaporation, furnished a second crop of crystals. Both crops when dry were treated with fuming nitric acid in the usual way; the crude bromindone was dissolved in alcohol and filtered to collect the quinone. The latter was collected on tared filters, washed with alcohol till free from all soluble matter, dried, and weighed. The results were:—

1st crop. 9·26 gram gave 0·05 gram quinone = 0·54 per cent.
2nd „ 4·27 „ 0·119 „ „ = 0·45 „

The yield of quinone from dibrom-α-naphthol may be taken as about 0·5 per cent. The difference in yield between the two fractions was not sufficient to render it hopeful that the quinone-yielding substance could be separated by crystallisation from petroleum.

The formation of monobrom-α-naphthaquinone was in the first place rendered probable, from the observation that the derivatives of a specimen of bromindone, obtained by the action of nitric acid somewhat under strength (1·462 sp. gr.), did not give correct results on analysis. Some of this preparation was brominated by allowing it to remain for some hours in glacial acetic acid solution containing excess of bromine. The crystalline cake which thus formed was removed, washed with acetic acid, and crystallised from the same solvent. The purified substance formed long, yellow, prismatic needles melting with partial sublimation at 216°, and softening a few degrees below this temperature. The substance crystallised from toluene in large, yellow scales, and when dry was easily sublimed by heating in a dry tube, the sublimate consisting of a woolly mass of fine, yellow needles. The compound was identified as dibrom-α-naphthaquinone, the melting point of this compound being given by Miller as 218° (*Ber.*, 1884, Ref. 355).

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* I will take the present opportunity of pointing out a discrepancy between our results and the work of Erdmann (*Annalen*, 247, 306), which is at present inexplicable, and for the clearing up of which a further supply of the quinone will be necessary. If the latter is, as the evidence seems to indicate, the peri-dioxynaphthalene, then the product of its reduction should have a similar constitution. Our dihydroxynaphthalene, however, differs in the melting point of its diacetate, and in other respects from the peri-derivatives described by Erdmann in the paper referred to. The dihydroxynaphthalene of this author melts at 137—138°, and its diacetate at 147—148°. The possibility of intramolecular change is, however, not excluded in the process by which Erdmann obtained these compounds; viz., by fusing the "sultone," $C_{10}H_6<\genfrac{}{}{0pt}{}{NH}{SO_2}$, with alkali.—R. M.

0·2273 gram gave 0·3184 gram CO_2 and 0·0345 gram H_2O.
0·1486 „ 0·1760 gram AgBr.
0·1793 „ 0·2138 „ „

	Calculated for $C_{10}H_4Br_2O_2$.	Found.	
C	37·97	38·20	
H	1·27	1·69	
Br..............	50·63	50·40	50·74

The anilide of the dibromoquinone (anilidobromonaphthaquinone) was also prepared, and, after crystallisation from glacial acetic acid, formed brilliant, red scales melting at 190° (Miller gives the melting point as 194°).

For the further identification of the compound, and with the object of contributing to its chemical history, the reduction-product was prepared by dissolving the substance in glacial acetic acid, and reducing with zinc-dust. On filtering the solution and diluting with water, white needles separated which, on exposure to the air, acquired a pink tint. The melting point was above 255°.

0·1436 gram gave 0·1735 gram AgBr.

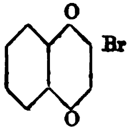
	Calculated for $C_{10}H_4Br_2(OH)_2$.	Found.
Br	50·31	50·72

On boiling this dibromodihydroxynaphthalene for a few minutes with excess of acetic anhydride and a little anhydrous sodium acetate, it forms an acetyl-derivative, which, after crystallisation from alcohol, forms white needles melting at 238°, and softening a few degrees below this temperature. The substance requires a large volume of boiling alcohol for its solution. Analysis showed that one acetyl-group had entered the molecule:—

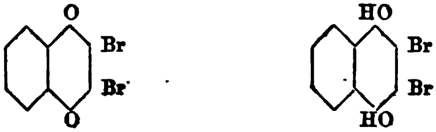
I. 0·2213 gram gave 0·3236 gram CO_2 and 0·0534 gram H_2O.
II. 0·2325 „ 0·3400 „ 0·0572 „
III. 0·1948 „ 0·2034 gram AgBr.

	Calculated for	Found.		
	$C_{10}H_4Br_2{\cdot}HO{\cdot}OC_2H_3O$.	I.	II.	III.
C	40·00	39·88	39·89	—
H	2·22	2·68	2·73	—
Br........	44·44	—	—	44·43

The formation of dibrom-α-naphthaquinone by the bromination of the crude product obtained by the action of nitric acid on dibrom-α-naphthol indicates that this product contains the monobrom-α-naphthaquinone—



The constitution of the dibrom-α-quinone and its reduction-product may be regarded as established—



The dihydroxy-derivative is, as might have been expected, phenolic in character, dissolving readily in cold aqueous alkali, but it is of interest to note that the replacement of one of the hydroxylic hydrogen-atoms by acetyl destroys the phenolic character, the monacetyl-derivative above described being insoluble in cold aqueous alkali.

Finsbury Technical College.

LVII.—*A New Method for the Estimation of Nitrates and Nitrites in Water.*

By R. Ormandy and J. B. Cohen, PhD., Owens College, Manchester.

The process, which we describe below, resembles that of Gladstone and Tribe, in which a zinc-copper couple is employed to decompose nitrates and nitrites into ammonia. We replace the zinc-copper couple by thin sheet aluminium, coated with a film of metallic mercury. We find, after careful comparative determinations, that this aluminium-mercury couple acts more rapidly than the zinc and copper, and gives equally good results. Nitrates in small quantities, such as occur in natural waters, are entirely reduced by the aluminium-mercury couple in about an hour, whereas the couple of Gladstone and Tribe requires about six hours to effect complete reduction. Most of the books which have reference to water analysis recommend the use of a solution of caustic soda and metallic aluminium to reduce the nitrates. It will be seen from our results, that this process is absolutely unreliable, unless certain special precautions are taken.

The aluminium was obtained from the Aluminium Company, at Oldbury, in the form of narrow foil about 2½ inches wide, a piece 5 inches long weighing about 1 gram. It dissolves in dilute caustic soda solution, leaving a small quantity of black residue. This residue is magnetic, and contains iron, aluminium, silicon, and carbon, probably in the free state, together with traces of copper and calcium. This residue has the curious property of becoming inflammable when heated, and burns with a bright flash, leaving behind a fused, black mass.

The aluminium foil is readily coated with mercury by shaking it in a solution of mercuric chloride (1 vol. of a saturated solution with 1 vol. of water) for about a minute. Metallic mercury adheres to the surface of the aluminium, and the couple, after being washed a few times with pure water, may be introduced into the water to be analysed.

This should be done without loss of time, as the couple very readily oxidises. The couple is left in contact with the measured quantity of water in the cold until the aluminium is converted into oxide. Water and precipitate are then transferred to the retort for distillation. The contents of the retort boil quietly and without bumping. In the course of more than 100 experiments, we experienced no inconvenience from the presence of the precipitate. The aluminium, as it comes from the works, is usually coated with an invisible film of grease, and this grease is acted upon by the couple, yielding very perceptible quantities of ammonia. Until we discovered this source of error, we had almost abandoned the method from the unaccountable discrepancies in the results.

When the aluminium is heated in a current of hydrogen, the grease is removed, and the aluminium retains no trace of nitrogen. The following results were obtained:—

No. of experiment.	Weight of foil used.	Water alone, parts per million of ammonia.	Water and Al-Hg couple, parts per million of ammonia.
1	0·5	0·012	0·014
2	0·1	0·012	0·014
3	0·2	0·028	0·026
4	0·2	0·032	0·026

We subsequently found that simply heating the foil in a Bunsen flame practically effected the same result. There is always a slight excess of ammonia when treated in this way; but the results scarcely exceed experimental error.

Weight of foil used.	Water alone, parts per million of ammonia	Water and Al-Hg couple, parts per million of ammonia.
grams		
2	0·010	0·020
2	0·012	0·020
2	0·014	0·022
2	0·014	0·018
2	0·018	0·020
2	0·014	0·016
2	0·014	0·020
2	0·016	0·020
2	0·012	0·014

The zinc-copper couple, made by depositing copper on the uncleaned surface of sheet zinc, gave off no trace of ammonia from the grease on its surface.

The action of the aluminium-mercury couple on nitrates was determined in the following manner. A weak standard solution of potassium nitrate was prepared, containing the equivalent of 0·01 gram of ammonia to the litre, and varying quantities of the solution submitted to the action of the couple in a partly closed flask until the aluminium (2 grams) had been converted into oxide. The whole contents were then transferred to the retort, and the ammonia determined by Nessler's reagent in the usual way. In this, and in every series of experiments, a sample of the distilled water used was tested side by side with the sample to which the couple had been added, so as to check any possible error arising from extraneous causes. The effect of the small quantity of ammonia found in the distilled water has been allowed for, and does not appear in the table.

No. of experiment.	Volume of KNO_3 solution used and diluted to ½ litre.	Equivalent of NH_3, in parts per million.	NH_3 found, parts per million.
	c.c.		
1	5	0·10	0·098
2	5	0·10	0·096
3	5	0·10	0·106
4	6	0·12	0·116
5	10	0·20	0·194

The results indicate that, with varying quantities of potassium nitrate, the method is perfectly accurate.

It is well known that albuminoïd substances undergoing decomposition split up into simpler organic nitrogen compounds, before free ammonia makes its appearance. It appeared to us important to determine whether the zinc-copper or aluminium-mercury couple effected any change in this direction, *i.e.*, hastened the decomposition and the formation of free ammonia when in contact with partially decomposed albumin. It is clear, that if this were the case a natural water containing partially decomposed albumin would, after the action of the couple, indicate a larger amount of nitrates or nitrites than was actually present in the original water. A long series of experiments was undertaken with this object. The method adopted was to allow dilute solutions of pure gelatin to stand for several days, until decomposition had proceeded for some time. Portions of the solutions were withdrawn every day, or on alternate days.

In one portion, the amounts of free ammonia and ammonia evolved after the further addition of caustic soda were determined.

Other portions were submitted to the action of the couples, and the amount of free ammonia and the ammonia given off after the addition of caustic soda determined.

We give here briefly the summary of our results.

1. Neither couple affects the amount of free ammonia produced during the decomposition of the albumin, that is to say, the amount of free ammonia given off each day by the decomposing albumin was the same, with or without the addition of the couple.

2. The addition of caustic soda to the albumin solution and to the solution with the zinc-copper couple set free an additional quantity of ammonia, which was the same in the two cases.

3. In the case of the albumin solution, acted upon by the aluminium-mercury couple, the amount of free ammonia produced by the addition of caustic soda was largely in excess of that in the other two solutions, as the following example shows. The solution had been standing for nine days:—

	Albumin solution, parts per million of ammonia.	Albumin solution after contact with Al-Hg couple, parts per million of ammonia.
Free ammonia	0·120	0·122
After addition of NaOH..	0·018	0·130

It is evident, therefore, that the aluminium couple acts upon the products of decomposition of the albumin, yielding other compounds, probably organic amido-acids, which are decomposed only on the addition of caustic soda. We intend to make a further study of the nature of these products.

LVIII.—*The Action of Zinc on Dilute Sulphuric Acid.*

By Frank Pullinger, B.A., B.Sc., late Scholar of Corpus Christi College, Oxford.

It has been known for many years that, whereas moist chlorine attacks sodium with great energy, the dry gas has little or no effect. And more recently it has been discovered that in order to burn carbonic oxide, carbon, sulphur, or phosphorus in oxygen, a trace of moisture is absolutely necessary. Indeed phosphorus may actually be distilled in oxygen if the gas be thoroughly dried (H. B. Baker, Trans., **47**, 1885, 349).

Other examples of this kind, in which a trace of a third substance is necessary for the interaction between two bodies, might be given. Thus Veley found that hydrogen sulphide has no action upon lime unless water is present; and Thorpe proved a similar effect in the case of the oxide of titanium.

But perhaps no more interesting case can be mentioned than the action of nitric acid upon various metals.

In 1874, Russell showed that nitric acid has no effect upon metallic silver in the absence of nitrous acid, and that with the increase of this substance in the liquid the velocity of dissolution is accelerated (Trans., 1874, 3). V. H. Veley has proved that if the nitrous acid is destroyed as fast as it is formed (say by urea), nitric acid has no action whatever upon copper (*Proc. Roy. Soc.*, **46**, 1889, 216). And a similar result has been observed in the case of certain other metals.

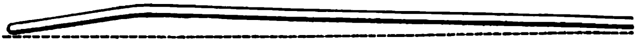
In view of these facts, it seemed interesting to conduct an investigation to discover whether in the case of sulphuric acid and the metals analogous effects could be proved. Zinc was the metal first selected, inasmuch as it was known that the purer the metal the less rapid is the action of sulphuric acid upon it.

In 1830, A. de la Rive showed that distilled zinc dissolves very much more slowly in dilute sulphuric acid than the commercial substance. He proved this to be due to the removal of other metals by the distillation—and particularly of iron. The dissolution of commercial zinc was ascribed to the formation of voltaic couples of zinc with the various impurities, and the strength of acid which acts most readily upon the metal was shown to be that which has the greatest electrical conductivity (*Ann. de Chim.* [2], **43**, 1830, 425). It thus seems very natural to suppose that *pure* zinc would be unacted upon by *pure* sulphuric acid, but that if a third substance be present, whether in the metal or in the acid, dissolution would be effected owing to the formation of an electric circuit.

Reynolds and Ramsay (Trans., 1887, 854) in 1887 found that, after preparing highly purified zinc by electrolysing the purified sulphate and subliming the product thus obtained *in vacuo*, "the sublimed metal . . . . was nearly unacted upon by sulphuric or hydrochloric acid."

Purification of the Zinc.

In this investigation the zinc used was prepared by distilling metal obtained from the makers as chemically pure, three times *in vacuo*. The distillation was effected in hard-glass tubes placed on a combustion furnace. The tubes were slightly bent towards their closed ends, and the open ends were joined up to an efficient water pump. The metal condenses in globules which on tapping the tube fall down and unite to form large masses. The globules on cooling develop facets, and are hardly acted upon by dilute sulphuric acid. The larger masses have generally a somewhat dirty appearance, and dissolve more rapidly, while the residue is still more dirty, and dissolves very quickly indeed. If the residue be further distilled, a point arrives when it loses its molten condition and becomes a greyish-black, spongy mass. This dissolves with extreme rapidity in a dilute acid and may, *at a higher temperature*, be completely distilled.

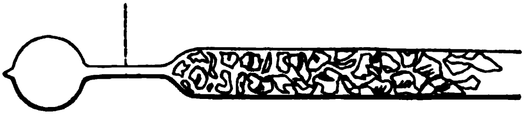


In the first instance, the distillation tubes were cleaned by a plug of cotton-wool and afterwards rinsed with boiling distilled water; but it was found that the distilled zinc adhered with such tenacity to the glass that it could not be removed without bringing with it a very thin, iridescent, glassy film. The majority of the tubes were therefore used uncleaned.

It should be mentioned that in selecting zinc for the second and third distillations the more volatile portions and the residues from preceding operations were rejected.

In order to obtain specimens of metal the areas of whose surfaces could be accurately determined, it was decided to cast the zinc into spheres. This was easily done by blowing a small bulb on the end of a piece of hard-glass tubing, placing fragments of zinc in the limb of the tube, and, after connecting the open end with a water pump, melting down the metal into the bulb. While the metal was still molten, the pump was disconnected, the inward pressure thus causing the bulb to be completely filled with metal. This operation prevents the formation of hollow spheres, which are otherwise produced. In this way, with a little care, spheres of zinc can be obtained which have a perfectly bright and lustrous appearance. In a purified acid they are nearly insoluble, and they appear to contain no trace of either lead or cadmium.

Capillary tube filtering the metal.



Purification of the Acid.

The first acid used was prepared by diluting "pure" sulphuric acid with three times its weight of water, heating the mixture strongly, and passing in air for 30 minutes. This length of time, however, subsequently proved to be insufficient; so in most cases the acid was heated for six hours in a flask provided with an inverted condenser. Hydrogen and carbon dioxide were also substituted for air—and with much better results, though the chief agent in the purification is simply heat, as will appear from the following table:—

Effect of Boiling Dilute Sulphuric Acid for Six Hours.

Gas used.	None.	H_2.	CO_2.	Air.	None, and no heat applied.
Grams of zinc dissolved in 30 mins.	0·003	0·004	0·005	0·008	0·020
Rel. den. of acid ...	1·186	1·177	1·179	1·189	1·182

In these cases the same zinc sphere was used. It weighed about 2·5 grams, and had a rough and coarse surface, produced by the prolonged action of acid in previous experiments. The amount of acid used was 25 c.c., and the temperature was 26° C.

In the tables next given, the contrast between the action of boiled and unboiled acids will also be apparent, and it will be seen that the strength of the acids, within narrow limits, does not materially alter the rate of dissolution. Thus unboiled acids, whether stronger or weaker than a given boiled acid, always act more vigorously than the latter. The influence of the nature of the surface of the metal must be noted in these experiments; it will be more carefully considered afterwards.

I.

(i.) Loss in 30 mins. in boiled acid of rel. den. 1·179 (hydrogen passed)	0·010	Freshly cast sphere. Surface fairly smooth. Weight 5 grams.
(ii.) Ditto ditto	0·014	Same sphere.
(iii.) Loss in 30 mins. in unboiled acid of rel. den. 1·157	0·054	Same sphere. The surface became very rough during the action.
(iv.) Loss in 30 mins. in same acid as in (i) and (ii)	0·037	Same sphere.

II.

(i.) Loss in 30 mins. in boiled acid of rel. den. 1·179	0·009	New sphere of smooth surface produced by action of *aqua regia*. Weight 3 grams.
(ii.) Loss in 30 mins. in unboiled acid of rel. den. 1·175	0·058	Same sphere. The surface became rough during the action.
(iii.) Loss in 30 mins. in same acid as in (i)	0·034	Same sphere.

III.

(i.) Loss in 60 mins. in boiled acid of rel. den. 1·179	0·005	New sphere with surface made smooth by action of *aqua regia*. Weight 1·25 grams.
(ii.) Ditto ditto	0·007	Same sphere.
(iii.) Loss in 30 mins. in unboiled acid of rel. den. 1·226	0·045	Same sphere. The surface became rough during the action.
(iv.) Loss in 30 mins. in same acid as in (i) and (ii)	0·027	Same sphere.

In all these cases 50 c.c. of acid were used, and the temperature was 26° C. The results prove clearly either (i) that sulphuric acid contains some impurity which accelerates the dissolution of zinc but which is totally or partly decomposed or driven off by boiling, or (ii) that some substance is formed by decomposition which retards the rate of dissolution. To ascertain the nature of this impurity, it was decided to determine the action of various sulphur compounds in accelerating or retarding the rate of dissolution; but before the results of these experiments are given it will be necessary to give a short account of the way in which the operations were carried out, and of the influence of the nature of the surface of the metal upon the reaction.

Mode of Experimenting.

An ordinary distillation flask was provided with a capillary delivery tube to collect the evolved hydrogen in the usual way at a pneumatic trough. It was placed in a water-bath of tinned iron, and this was kept at a constant temperature by means of a Harcourt's gas regulator.[*] The acid was placed in the flask, and, when it had attained the temperature of the bath, the sphere of zinc was introduced. In some cases the volume of gas evolved in a given time was considered, in others the weight of zinc dissolved.

Influence of the Nature of the Metallic Surface.

In 1866, Calvert and Johnson noticed "the irregularity of the action of sulphuric acid on zinc, depending . . . . upon the peculiar state of its surface." "Thus we have found," they say, "that cubes, which had been made of the same zinc but at different times, were acted upon more or less by the same acid when placed under the same circumstances; and these observations gradually led us to the discovery of a curious fact, viz., that a perfectly clean surface of zinc will become after a few days sufficiently oxidised by contact with air to modify in a very marked degree the action of sulphuric acid upon it. Thus, if a cube of zinc recently filed is placed in sulphuric acid diluted with nine equivalents of water, the action may be considered as null; whilst if the same cube be gently heated in contact with air and allowed to cool, and be then placed in the same strength of acid, the attack is ten times greater" (Trans., **4**, 1866, 434). From what follows in this paragraph it will be tolerably evident that roughness, not oxidation, of the metallic surface is the *vera causa* of the increase of velocity. Indeed, it is difficult to see how superficial oxidation could exert more than a momentary influence, seeing that the oxide would be instantly dissolved by contact with the acid; whereas increased roughness produced by the formation and subsequent dissolution of the oxide would, as is here shown, increase the rate of dissolution of the metal very materially.

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[*] See paper by V. H. Veley, *Chem. Soc. Trans.*, 1883, p. 370.

Experiment 1.—A large zinc sphere, weighing 8·5 grams, and cast in the way mentioned above, was taken. The surface was rubbed with sand-paper to ensure roughness, and the sphere was then dropped into 150 c.c. of sulphuric acid which had been boiled for one hour only during the passage of air. The relative density of the acid was 1·231, and its temperature during the action 23—24·5°. In one hour 0·7935 gram of zinc was dissolved and 275·9 c.c. of moist hydrogen obtained. The rate of dissolution is here, of course, extremely great, and so in the next experiments spheres were taken which had been cast in glass bulbs, but which had not been rubbed with sand-paper.

Experiment 2.—A sphere weighing 3·2 grams was used under almost the same circumstances as in the last experiment. In the first few moments the evolution of gas was extremely slow; in 20 minutes only 15·2 c.c. were collected. Then, as the surface became coarser, the rate of dissolution increased, and in two consecutive periods of 20 minutes there were collected 28·4 and 40·4 c.c. of gas. It should here be mentioned that as a zinc sphere of smooth surface dissolves, it first assumes a faceted structure, owing to the crystalline nature of the metal, and afterwards becomes very coarse indeed, developing a pitted or pimpled surface.

Experiment 3.—Four spheres were taken and dropped into 50 c.c. of acid under the same circumstances as before. Of these, A was much smoother than B, and C than D. Making some allowance for the small difference in the areas of surface of each, it will be perfectly obvious that the smoother the sphere the slower is the rate of dissolution:—

	Weight.	C.c. of gas evolved in 15 mins.
A....................	2·967	7·4
B....................	2·981	15·0
C....................	3·393	7·0
D....................	3·317	11·1

Experiment 4.—An acid of rel. den. 1·178 was now used. It had been boiled for six hours while hydrogen was passed through it. Into 50 c.c. was placed a very bright sphere weighing 2·8 grams. In one hour and a half only 0·0025 gram was dissolved.

At this point it was discovered that the best way to obtain a perfectly smooth metallic surface is to act on the sphere with aqua regia. A cast sphere is simply dropped into a mixture of concentrated nitric and hydrochloric acids. A violent effervescence occurs, and after 10 or 15 seconds the action is stopped by adding a large excess of water. After well washing and drying, the specimen is ready for use.

A sphere thus prepared, and weighing 1·8 grams, lost in 19 hours 40 minutes merely the small weight of 5 milligrams when placed in the boiled acid just mentioned.

Another sphere, weighing 2·8 grams, lost only 6 milligrams in 19 hours 25 minutes.

All spheres which had been rubbed with sand-paper dissolved with rapidity under the same conditions.

From these experiments, it is evident that *dilute sulphuric acid has little or no action upon zinc*, provided that the acid be boiled for several hours and the metal have a perfectly smooth surface.

Action of Various Sulphur Compounds.

Hydrogen Sulphide appears, like all the sulphur compounds tried, to have no action in either accelerating or retarding the dissolution of the zinc. A few results will be given.

Experiment 1.—A smooth sphere, weighing 2·9 grams, was dropped into an acid of rel. den. 1·231, which had been boiled for an hour during the passage of air. The temperature was 22° C. In three successive periods of five minutes there were evolved 0·0, 3·2, and 4·2 c.c. of hydrogen. 10 c.c. of the same acid, through which hydrogen sulphide had been passed, were then added, and the rate became 5·2 and 5·6 c.c. for five minutes. After adding more hydrogen sulphide, the rate became 7·7 and 7·9 for five-minute intervals, and after more still, 7·7 and 8·1. This gradual increase in the rate is, of course, due to the surface of the metal becoming roughened during the progress of the reaction.

Experiment 2.—A rough sphere, weighing 3·3 grams, was dropped into the same acid at a temperature of 23° C. For periods of five minutes there were evolved 9·6, 9·8, 9·8, 10·4 c.c. of gas, and after adding hydrogen sulphide, 10·7, 10·0, 10·3, 9·6 c.c.

Sulphur Dioxide.—A large number of experiments was made with this substance, as it was thought that it might perform an active part in the dissolution, just as nitrous acid does when copper is dissolved in nitric acid.

Experiment 1.—A rough sphere, weighing about 3·5 grams, was placed in the acid just mentioned at a temperature of 22° C. For five-minute periods there were evolved 11·4, 11·6, 12 0, 12·4 c.c. of hydrogen, and after a few drops of a solution of sulphur dioxide had been added, 12·4, 11·6, 11·6, 13·5, 12·3, 12·2.

Experiment 2.—When much sulphur dioxide is present, the evolution of hydrogen almost ceases, but the rate of dissolution remains about the same. Thus, under the same circumstances as in the last experiment, a rough sphere, weighing about 2 grams, lost 0·099 gram in 15 minutes, the evolution of hydrogen being regular (12·2, 11·3, 12·0 c.c. for five-minute periods). Then, after the addition of sulphur dioxide, the sphere lost 0·085 gram in the same time, while the evolution of hydrogen became much slower.

When smooth spheres are used, the acceleration of the velocity of dissolution, after adding sulphur dioxide, is not greater than can be accounted for by the increasing roughness of the surface of the zinc.

With acids boiled for six hours, the results are precisely the same. Thus, a smooth sphere in an acid of rel. den. 1·178 lost practically nothing in one hour, and only 2 milligrams in the same time when a few drops of a solution of sulphur dioxide had been added.

Hyposulphurous acid, contained in an aqueous solution of sulphur dioxide which had stood in contact with pure zinc for a short time, also proved to have no effect, as will be seen from the table (p. 823).

Influence of Hydrogen Peroxide.

Experiment 1.—An acid of rel. den. 1·179, which had been boiled for six hours during the passage of hydrogen, was taken. At a temperature of 26° C. a rough sphere, weighing about 3 grams, lost 0·034, 0·036, 0·037 gram in half-hour periods. After the addition of 5 c.c. of the same acid, which had stood in contact with barium dioxide and been filtered, the losses were 0·050 and 0·047 gram. In an unboiled acid of rel. den. 1·172, the loss in the same time was 0·193 gram.

Experiment 2.—Here an acid of rel. den. 1·231, which had been boiled for an hour only during the passage of air, was used. For five-minute periods, a rough sphere, weighing about 7 grams, gave 16·0, 14·0, 16·0, 14·0 c.c. of hydrogen, and after the addition of hydrogen peroxide, 23·5, 24·5, 28·5, 28·5.

Another sphere, weighing 8 grams, gave 11·4, 12·0, 12·6, 12·8 c.c. of gas, and after adding the peroxide, 16·2, 15·4, 16·6, and 19·8. The temperature in these cases was 22° C.

Experiment 3.—In one case, using a boiled acid of rel. den. 1·178, the rate was nearly doubled after adding hydrogen peroxide. For five-minute intervals the amount of gas collected was 3·3, 2·7, 2·2, 2·2 c.c., and after the addition of the peroxide 3·7, 3·7, 4·6, and 5·0.

From these experiments, it will be seen that hydrogen peroxide

	Acid used (50 c.c.).	Zinc dissolved (in grams).	Hydrogen evolved in 5 min. periods.	Size of sphere.	Surface of sphere.	Temperature.
1	Unboiled, rel. den. 1·231	0·070 in 20 mins.........	6·9, 6·7, 6·0, 6·0	4·3 grams	rough	22·5°
2	Same, but with a few drops of H_2SO_2	0·080 in 20 mins.........	—	same	same	same
3	Boiled, rel. den. 1·178	0·001 in 40 mins.........	—	1·3 grams	smooth	23·0°
4	Same, but with a few drops of H_2SO_2	0·004 in 40 mins.........	—	same	same	same

Wackenroder's solution has also no effect :—

	Acid used (50 c.c.).	Zinc dissolved (in grams).	Hydrogen evolved in 5 min. periods.	Size of sphere.	Surface of sphere.	Temperature.
1	Unboiled, rel. den. 1·231	0·122 in 20 mins.........	11·1, 10·5, 10·8, 11·0	3·9 grams	rough	22·5°
2	Same, but with a few drops of Wackenroder's solution..................	0·116 in 20 mins.........	11·6, 10·4, 10·2, 9·8	same	same	same
3	Boiled, rel. den. 1·178	0·001 in 30 mins.........	—	1·3 grams	smooth	23·0°
4	Same, but with a few drops of Wackenroder's solution..................	0·000 in 30 mins.........	—	same	same	same

materially augments the rate of dissolution of zinc in sulphuric acid.

Action of an Electrolysed Acid.

The oxidising action which goes on during electrolysis increases the power of the acid in dissolving zinc.

Experiment 1.—A smooth sphere, weighing over 2 grams, was acted upon by an acid of rel. den. 1·222, which had been boiled for six hours while hydrogen was blown through it. At a temperature of 24° it lost 0·012 gram in 1 hour 15 minutes. It was then placed (under similar conditions) in the same acid which had been electrolysed for 25 minutes, and in 1 hour 15 minutes it lost 0·466 gram. Of course, allowance must here be made for increased roughness produced during the reaction, but in any case the action of the electrolysed acid must have been much more powerful than that of the acid which had been merely boiled.

Experiment 2.—A rough sphere, weighing 1 gram, was placed in a boiled acid of rel. den. 1·186 for 15-minute periods at a temperature of 28° C.

	Acid of sp. gr. 1·186.	Loss in 15 mins.
(i.)	Boiled for six hours	0·004 gram.
(ii.)	Ditto	0·004 ,,
(iii)	Ditto	0·004 ,,
(iv.)	Do., and electrolysed for 20 mins.	0·048 ,,
(v.)	Boiled for six hours	0·016 ,,
(vi.)	Do., and electrolysed for 20 mins.	0·059 ,,
(vii.)	Boiled for six hours	0·023 ,,
(viii.)	Ditto	0·016 ,,
(ix.)	Ditto	0·009 ,,
(x.)	Ditto	0·008 ,,

From the figures here given, a somewhat curious fact comes to light. It was noticed throughout the whole of the experiments that each acid seems to impress a more or less constant condition of surface upon the spheres. An unboiled acid acts with great rapidity, and forms a very rough surface. A boiled acid acts less quickly, and forms a more even surface. On referring to Experiments vii—x, however, it will be seen that a considerable time is required before an acid can restore its original condition of surface to a sphere, after that condition has been disturbed.

Action of Nitric Acid.

Only one experiment with nitric acid was made, and it was found that a very small quantity of it greatly increased the rate of dissolution. A rough sphere, weighing 2·607 grams, was placed, at a temperature of 22·5° C., into 50 c.c. of a dilute sulphuric acid, which had a rel. den. of 1·231, and which had been boiled for one hour during the passage of air. The rate of dissolution was uniform, 6·0, 6·4, 6·0, and 5·6 c.c. of gas being collected in five-minute intervals. The loss in 20 minutes was 0·067 gram. Four or five drops of pure nitric acid were then added, and the loss in 20 minutes increased to 0·181 gram, or nearly three times as much as in the first case. The evolution of gas almost entirely ceased.

Action of Hydriodic Acid.

Experiment 1.—A rough sphere, weighing 3 grams, was placed in the same acid as that used in the last experiment, and under similar conditions. For five-minute periods there were evolved 7·0, 6·8, 7·4, 6·5, 6·4, 6·3 c.c. of hydrogen, and after adding a few drops of a pure solution of hydriodic acid, the rate became reduced to 2·8, 1·7, 2·0, 1·8, 2·0, 2·0 c.c. of gas.

Experiment 2.—A rough sphere, weighing 2·5 grams, was placed in an acid which had been boiled for six hours during the passage of hydrogen, and which had a rel. den. of 1·179. Three drops of a solution of hydriodic acid were added to 25 c.c. of the boiled acid, and the mixture, before the introduction of the zinc, had stood for several hours in a closed vessel in the dark. In 20 minutes the sphere lost 0·002 gram. Under similar conditions, but in a mixture containing more hydriodic acid, the sphere lost only 0·002 gram in 3 hours 33 minutes.

From this it is evident that dilute sulphuric acid containing a little hydriodic acid is almost without action upon zinc, even when the surface of the metal is extremely rough.

Nature of the "Third Substance."

The above experiments seem to show that ordinary, so-called pure sulphuric acid contains some substance (probably in small quantity) which is wholly or partly decomposed or driven off by boiling. This substance is not hydrogen sulphide nor sulphur dioxide, and it is not hyposulphurous acid, nor any of the acids contained in Wackenroder's solution.

From the fact that oxidising agents, such as hydrogen peroxide, hydrogen nitrate, and sulphuric acid which has been electrolysed increase the velocity of dissolution, it is not improbable that the third substance is some highly oxygenated compound. This view is borne out by the action of hydriodic acid, a reducing agent which very greatly retards the rate of dissolution. And the fact that "pure" sulphuric acid, when diluted with four times its volume of water, reacts with a solution of potassium iodide and starch also favours the hypothesis.

From the great action of nitric acid in increasing the rate of dissolution, it might well happen that a mere trace contained in sulphuric acid would be sufficient to commence the reaction. But all specimens of the acid, when tested with brucine, gave negative results, although a very pale rose tint was always obtained, even on boiling down several times acids which had been largely diluted (Fresenius, "Qualitative Analysis," 10th edition, p. 231). The acids were also tested for nitrous acid by means of metaphenylenediamine, but seemed to contain not even a trace. Hydrogen peroxide was also absent, and it was not formed on heating, as in McLeod's electrolysed acid mentioned below.

Sulphurous acid was probably present in small quantities, as all the acids decolorised to a slight extent a solution of potassium permanganate. The boiled acids gave this reaction, even in a stronger degree than the unboiled.

An attempt was made to prepare *pure* sulphuric acid by oxidising a solution of sulphurous acid with hydrogen peroxide; but the acid thus made still dissolved zinc. Copper sulphate was next precipitated with hydrogen sulphide, and the resulting liquid distilled several times in a glass retort; this acid also dissolved zinc, and liberated iodine from potassium iodide, but it did not seem to decolorise permanganate.

The view here put forward is, that the third substance which causes the dissolution of the zinc is persulphuric acid. McLeod remarks that on submitting dilute sulphuric acid to electrolysis, an oxidising agent is produced which liberates iodine from potassium iodide, but which is not peroxide of hydrogen. He believes it to be persulphuric acid, whose anhydride was obtained by Berthelot when electric sparks were passed through a mixture of oxygen and sulphur dioxide. On boiling the liquid containing this acid, hydrogen peroxide was produced (McLeod, *Chem. Soc. Trans.*, 1886, p. 594).

The facts established in this paper agree well with the supposition that persulphuric acid is the *vera causa* of the dissolution of zinc in sulphuric acid. And especial mention may be made of the following results:—First, that the acids used had always much less action on zinc, when they had been boiled (the persulphuric acid being decomposed by the heat); second, that an electrolysed acid acts much more readily than an acid which has not been submitted to that process; third, that hydrogen iodide prevents the reaction almost completely, even under circumstances which are most favourable to the reaction; fourth, that ordinary "pure" sulphuric acid contains some body which, like persulphuric acid, liberates iodine from potassium iodide, but which is not hydrogen peroxide; fifth, that other highly oxygenated compounds, such as nitric acid and hydrogen peroxide, act in the same way as persulphuric acid, if that is, indeed, the body contained in sulphuric acid which has been electrolysed.

Summary and Conclusion.

The following results have been proved in this paper:—

(i.) That pure zinc with a perfectly smooth surface is not acted upon by dilute sulphuric acid which has been submitted to prolonged boiling.

(ii.) That pure zinc with a rough surface is readily acted upon, but in a less degree by acids which have been boiled than by those which have not.

(iii.) That oxidising agents, such as electrolysed sulphuric acid, hydrogen peroxide, and nitric acid, increase the rate of dissolution.

(iv.) That a reducing agent, such as hydriodic acid, almost entirely prevents dissolution, but that those containing sulphur, such as sulphur dioxide, are without effect.

(v.) That it is not improbable that when zinc with a rough surface dissolves in dilute sulphuric acid, persulphuric acid acting catalytically is the cause of dissolution.

(vi.) That, in all probability, *pure* dilute sulphuric acid would, at ordinary temperatures, be entirely without action upon metallic zinc, whether the surface of the latter were rough or smooth.

In conclusion, I must express my very sincere thanks to Mr. V. H. Veley, M.A., of the Oxford University Museum. It was he who proposed this work, and from him, during its progress, many valuable suggestions and much help were obtained.

I am also greatly indebted to Professor Odling and Mr. W. W. Fisher, M.A., for permission to carry on this work in the University Laboratory.

LIX.—*A New Monobromocamphor.*

By J. E. Marsh.

Action of Bromine on Camphor.

The action of bromine on camphor may be said to be a commercial process for the production, for pharmaceutical purposes, of the ordinary monobromocamphor. The yield of the bromocamphor is, in the first instance, a relatively small one. There accompanies the crystalline bromocamphor a considerable quantity of an oil which, according to Swarts, is the hydrobromide of bromocamphor,

$$6C_{10}H_{15}BrO + HBr.$$

By distilling this oil, the yield of bromocamphor is, as is known, materially increased. The existence of such a compound as that supposed by Swarts is open to serious doubt. In the first place, it is unlikely that bromocamphor should form a compound with hydrobromic acid, and still less likely that 6 mols. of the one should combine with 1 mol. of the other. I shall endeavour in this paper to show that the action of bromine on camphor is such as to give two isomeric monobromocamphors. These are in approximately equal quantity, of which one, the iso- or β-bromocamphor, is readily converted by distillation, under ordinary pressure, into the other, namely, the ordinary or α-bromocamphor; and the increased production of the α-bromocamphor by distilling the above-mentioned oil is to be explained by the conversion of the β- into the α-isomer.

Preparation of the Iso- or β-Monobromocamphor.

The new isomer is best prepared by the action of bromine on camphor in presence of alcohol, the diluent alcohol, which was also employed by Swarts, appearing to facilitate the subsequent separation of the two isomers. This separation is in any case a difficult one, and I am unable to state positively that I have obtained the new isomer absolutely free from the ordinary modification. This I judge from the slight variations which specimens of the same melting point show in respect of rotatory power, or, perhaps it would be more correct to say that a slight admixture of the ordinary isomer affects the melting point much less than the rotatory power.

The β-isomer is extremely soluble in alcohol, and is separated from the α-modification by fractional crystallisation from alcohol. It is further separated from unaltered camphor by distillation *in vacuo*, when it distils unaltered at about 130° under 10 mm., or 140° under 20 mm. pressure. The α-isomer distils under the same circumstances at substantially the same temperature.

When bromine acts on camphor in presence of alcohol, the substitution appears to take place at once, regularly and quietly, without the formation, and subsequent decomposition at a high temperature, of the additive compound $C_{10}H_{16}OBr_2$. Whereas, when bromine acts on camphor alone, the additive compound formed at first decomposes, as is known, on raising the temperature, with some violence and with evolution of torrents of hydrobromic acid. The new isomer is also formed by this latter method, and at the same time I have obtained a liquid of boiling point about 160° under 20 mm. pressure, apparently a single substance, which contains an amount of bromine just midway between mono- and di-bromocamphor.

Estimation of Bromine.

Found.		Calculated for	
I.	II.	$C_{10}H_{15}BrO$.	$C_{10}H_{14}Br_2O$.
42·7 p. c.	42·7 p. c.	34·6 p. c.	51·6 p. c.

I hope to return to the investigation of this substance.

Properties of β-Monobromocamphor.

The β-monobromocamphor, as obtained after distillation in vacuo, forms on solidifying an almost transparent mass, easily breaking up into a soft, granular powder, very different in appearance from the hard crystals of the ordinary modification. It melts about 61° C. I have obtained it crystallised from dilute alcohol in feathery crystals which bind together when dry, forming tough, camphor-like masses. It is very soluble in alcohol, chloroform, carbon bisulphide, petroleum spirit, and glacial acetic acid, and separates on evaporation in the crystalline form.

It is volatile in the steam from boiling water, as is also the ordinary isomer.

It rotates the plane of polarised light to the right, but to a much less extent than the α-modification. I have found in alcoholic solution, $[\alpha]_D = +34{\cdot}9°$ and $+40°$, while the ordinary modification gives $[\alpha]_D = +139°$ (De Montgolfier).

Determination of Bromine.

I have made several determinations of bromine in the new substance, of which the theoretical percentage is 34·6. A specimen prepared with alcohol as a diluent, and distilled *in vacuo* and rotated

+34·9° gave 35·3 and 35·5 per cent. of bromine. It might, during the distillation, have mechanically enclosed some hydrobromic acid. Another specimen which had been crystallised from alcohol gave 35·1 per cent. Swarts' compound of 6 mols. bromocamphor and 1 mol. of hydrobromic acid requires 38·1 per cent. of bromine.

Distillation of β-Monobromocamphor under Ordinary Pressure.

When distilled under ordinary pressure, the new isomer begins to boil at 250°, and distils fairly constant at 265°; the distillate crystallised from alcohol gives the hard crystals characteristic of the ordinary modification, and melting about 76°. During the distillation there is a slight evolution of HBr, and a small carbonaceous residue is left in the retort. The conversion of one isomer into the other by distillation is not complete, and a more detailed examination was made as to the extent of the change.

A specimen of the isomeric β-bromocamphor, which had been distilled *in vacuo* and gave a specific rotation of +34·9°, was distilled slowly under ordinary pressure; the distillate gave now a specific rotation of +96°. Subjected to a second distillation, the new distillate gave a specific rotation of +98°. The distillate was dissolved in alcohol, and gave crystals of the ordinary modification and of specific rotation +135°, while on further evaporation a residue was obtained of specific rotation +56°; this residue again distilled gave a distillate* of specific rotation +76°. The alcoholic solution, on boiling down again, gave a crystallisation closely resembling the ordinary monobromocamphor.

It is thus evident that the β- is converted into the α-modification by distilling at ordinary pressure, while no change is effected by distilling *in vacuo;* that this change in any case is not complete, but would probably become so by separating the already formed α-isomer after each distillation.

Nature of the Isomerism and of the Isomeric Change.

The relations subsisting between the two isomeric bromocamphors render it extremely probable that we have here another instance, not of structural but of geometrical isomerism. The conversion of one isomer into the other by the action of heat recalls the similar conversion in the case of lævocamphoric acid and of fumaric acid. That the bromine-atom in the ordinary bromocamphor is attached to he carbon-atom, which is united to the CO-group, is rendered evident from the oxidation of this body to camphoric acid. The formula then which I have given for camphor (*Proc. Roy. Soc.*, **47**, 6) accounts perfectly for two stereographically isomeric monobromocamphors, and they may be represented by the condensed formulæ

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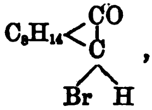
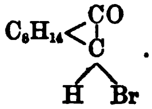
* On removing this substance from the desiccator, it was accidently moistened with strong sulphuric acid. It was, however, immediately recovered, not being in contact with the acid many seconds, and suffered no apparent change.

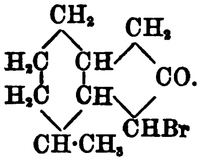


$$C_8H_{14}<\begin{matrix}CO\\|\\C\\\diagup\ \diagdown\\Br\quad H\end{matrix},$$



$$C_8H_{14}<\begin{matrix}CO\\|\\C\\\diagup\ \diagdown\\H\quad Br\end{matrix}.$$

and they will both have the same structural formula represented by

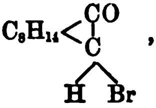


As to the particular space symbol which belongs to each isomer, we have no direct evidence; but it seems probable, from analogy, that the more stable of the two, namely, the ordinary bromocamphor, will be the one in which the bromine approaches more nearly the positive hydrocarbon groupings. The hexamethylene ring does not lie in the same plane with the pentamethylene ring, but inclined to it at an angle. The bromine-atom in the ordinary α-bromocamphor will then lie on the same side of the pentamethylene ring plane as the hexamethylene ring, while in the β-isomer the bromine-atom will be on the other side.

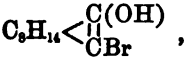
As to the mode in which the isomeric change is effected, Wislicenus has, in his well-known memoir, "Ueber die räumliche Anordnung, u. s. w.," attempted to explain the conversion of one stereometric isomer into the other in the case of the olefine-derivatives, by supposing the double linking to open out: then an exchange of groups occurs, the double linking is again formed, and the isomeric body obtained.

Von Baeyer has pointed out the objection to this view in the case of the hexahydroterephthalic acids, where there is no double linking. The same objection would apply to an isomeric change of this nature in the camphor series. Now these isomeric changes only occur, so far as is yet known, in cases where there is an oxygen-atom doubly linked to carbon, and situated in one of the groups which govern the isomerism. It may be, then, that this oxygen-atom, under the influence of heat or of certain reagents, passes into its unstable hydroxyl form, and, on returning to its original carbonyl state, gives not the original substance, but its isomer.

Thus we should have, in the case of the bromocamphors,

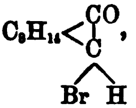


β-Bromocamphor.



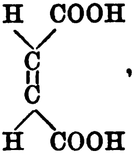
$$C_8H_{14}\Big\langle\begin{array}{l}\mathrm{C(OH)}\\ \|\\ \mathrm{CBr}\end{array}$$

Unstable transition compound.

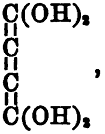


α-Bromocamphor.

and similarly, in the case of maleic and fumaric acids,

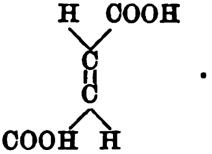


Maleic acid.



$$\begin{array}{l}\mathrm{C(OH)_2}\\ \|\\ \mathrm{C}\\ \|\\ \mathrm{C}\\ \|\\ \mathrm{C(OH)_2}\end{array}$$

Unstable transition compound.



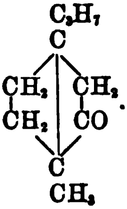
Fumaric acid.

The possibility of such isomeric change would then be confined to bodies which contain doubly-linked oxygen (or its equivalent, *e.g.*, sulphur or the imidogen radical) capable of yielding an unstable transition compound. These views, though they have been for some time in my mind, I cannot claim priority for, as E. Beckmann (*Annalen*, **250**, 365) has published a precisely similar explanation of the isomeric change in the case of the menthones. Dr. Beckmann, however, does not appear to have considered the far-reaching consequences to which his happy conception leads.

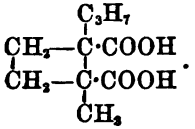
Note on the Constitution of Camphor.

Dr. Bamberger has published formulæ for camphor and camphoric acid (*Ber.*, **23**, 218), and believes that the latter is "wie es wohl meist angenommen wird"—a tetramethylene-derivative. Dr. Bamberger may possess some special information that his view has been generally accepted, but unfortunately he gives no references.

The formula which Dr. Bamberger gives for camphor is identical with that previously proposed by Wallach (*Annalen*, **230**, 269). It is a little difficult to interpret.



Does the formula represent simply an unsaturated derivative of hexamethylene, or does it represent two tetramethylene rings? In the latter case there is no special reason for retaining a hexagonal form, and the formula is without any analogy among synthetic compounds. That alone would not be sufficient to condemn it. The condemnation lies in the formula for camphoric acid derived from the above camphor formula. This formula represents camphoric acid as a tetramethylene derivative,



$$\begin{array}{ccc} & & C_3H_7 \\ & & | \\ CH_2 & - & C\cdot COOH \\ | & & | \\ CH_2 & - & C\cdot COOH \\ & & | \\ & & CH_3 \end{array}.$$

We have no evidence that camphoric acid is a tetramethylene-derivative. On the other hand, we have evidence that it is a hexamethylene-derivative, in that it yields, on hydrolysis, carbonic acid and hexahydroxylene—

$$C_{10}H_{16}O_4 = 2CO_2 + C_6H_{10}(CH_3)_2.$$

Further, if camphoric acid has the tetramethylene formula, then it is also a substituted succinic acid, and should yield a fluorescent compound with resorcin. I have not been able to obtain any such fluorescent body from camphoric acid.

A Sulphonic Acid of Monobromocamphor.

In conclusion, I may add that I have obtained a sulphonic acid by treating the ordinary bromocamphor dissolved in chloroform with chlorosulphonic acid. Neither the barium nor potassium salt appears to crystallise; the potassium salt forms on evaporation a syrupy product which, when dried at over 100°, gives a yellowish, very deliquescent powder. The bromine and sulphur in this were determined, and agree very fairly with the formula. Thus:

Per cent. sulphur found .... 9·51 p. c. and 9·33 p. c.
Calculated for $C_{10}H_{14}BrOSO_3K$...... 9·17 „

I hope to investigate the substance further.

University Laboratory, Oxford.

LX.—*Invertase: a Contribution to the History of an Enzyme or Unorganised Ferment.*

By C. O'Sullivan, F.R.S., and Frederick W. Tompson.

CONTENTS.

PAGE

Part I.—*General and Introductory.*

Objects of the Work 835
Literature referring to Invertase 836
Mode of Procedure 838

Part II.—*The Action of Invertase on Cane-Sugar.*

Rapidity of the Reaction 843
Influence of the Proportion of Invertase present 847
Influence of the Concentration of the Solution 849
Influence of Temperature 850
Influence of Foreign Substances 852
Molecular Weight of Cane-Sugar undergoing Inversion 861
Extent of the Power of Invertase 864
Comparison of the Laws governing Inversion with Harcourt's Laws .. 864
Method of Estimating and Recording the Activity of Preparations of Invertase 865

Part III.—*The Preparation of Invertase.*

Liquefaction of Yeast 869
Separation of Invertase from Yeast Liquor 875
Separation of the Ash 882
Purification of Invertase 884
Yeast Albuminoïd 886

Part IV.—*The Invertan Series.*

Splitting up of Invertase 887
Yeast Albuminoïd derived from Invertase 892
α-Invertan 894
β ,, or Invertase 896
γ ,, ... 901
δ ,, ... 903
ε ,, ... 904
ζ ,, ... 908
Molecular Weight of ζ-Invertan 911
Absorption Spectrum of ζ-Invertan 912
Action of Boiling Sulphuric Acid on Invertan 912
η-Invertan 913
Invertan Copper Compounds 914
Summary of the Invertan Series 916

Part V.—*Theoretical.*

Theory of Inversion by Invertase 918
Constitution of the Invertan Series 921
Part VI.—*Summary* 926

PART I.—GENERAL AND INTRODUCTORY.

Objects of the Work.

THE group of bodies known as unorganised ferments or enzymes are, as far as the products of their action are concerned, well defined; but, notwithstanding much useful and valuable work, we know very little of their mode of action and far less of their chemical constitution. They are a highly interesting and important class of substances, and are named unorganised ferments in contradistinction to the living or organised ferments, because they possess a life function without life. The function or functions of the organised ferments are highly complicated, while the function of the unorganised ferments is more or less a simple breaking down of some organic compound. They may be properly called *the transforming* ferments, for their function is a transforming or breaking down of one substance into two or more others. They may be looked upon as the reagents of life, and they are all products of it. Their function is a life function. Is there anything in this which can be distinguished from ordinary chemical action? If so, what?

Roberts, in his admirable little work on "The Digestive Ferments," holds that the living organism by which they are produced imparts to them a certain definite amount of vital force. This force is stored up in the ferment until it comes in contact with the particular substance upon which it is intended to act, and then it is used in altering it. This it continues to do until the whole of the vital force is exhausted. When this happens the ferment is still left—but it is dead.

Other observers think that the action of the enzyme is an ordinary chemical reaction, the ferment being either destroyed in the process, or remaining uninjured as in catalytic reactions.

To throw some light on these points was one of the objects of this work; the other was to arrive at some knowledge of the chemical constitution of the active substance. The generally received idea is that they are the products of some change in albuminoïds, but Hartley has shown that some of them at least do not act upon the spectrum in the same way as albuminoïds; and the published analyses represent them as containing far less nitrogen than that generally yielded by those bodies.

Of the many members of this class of compounds there are few that can be easily prepared in any quantity, and very few the function of which can be followed with moderate ease and sufficient accuracy. Our choice of material fell upon *invertase*, or, as it is often called, invertin. We prefer the former name, because we consider the ending (*ase*) should be the distinguishing affix of the names of this group. The reasons that we chose invertase were that we succeeded in discovering a method by which it is to be obtained in abundance, and because its function can be followed with ease and precision. We hope that the light thrown upon the mode of action and chemical constitution of one member of the group will be a key to a wider knowledge of the others.

Literature referring to Invertase.

Invertase has been the subject of a considerable amount of study, but the following may be taken as the principal published results on the subject:—

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We may briefly summarise these results.

Occurrence.—Beer yeast and, probably, all the saccharomycetes contain invertase. Hansen mentions several other micro-organisms in which it is present. Probably all organisms which have the power of assimilating cane-sugar contain invertase, though Hansen states that *Monilia candida* is an exception to this rule.* Bernard, and afterwards Brown and Heron, found it in the small intestine of the dog, pig, rabbit, rat, and various other animals, and the latter in the cold-water extract of malt. Kosman found it in the buds and leaves of young trees.

Preparation.—Beer yeast has always been the source of the preparation of invertase. The following are the principal methods used, but it does not seem that any of them yield more than very small amounts of the ferment.

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* We think it probable that if this organism were placed in a very slightly acid solution of cane-sugar and the whole heated to a temperature of 55° C., this apparent exception would disappear.

Yeast is killed with a little ether, and then the invertase is easily extracted by water and precipitated by alcohol (Hoppe-Seyler). It may be extracted from washed yeast by means of glycerine (Gunning). Yeast is washed with alcohol, dried, and powdered; then extracted with water, and the filtrate shaken up with ether, which causes the invertase to separate in a frog-spawn-like mass. This is extracted with water, and the ferment thrown out of solution by alcohol (Zulkowsky and König, and also Donath). Yeast, dried and powdered, is heated at 105° for six hours, then extracted with water, and precipitated by alcohol. Barth thus obtained about 0·4 per cent. of the yeast as *invertase.* Yeast is simply extracted with water, and sometimes the invertase is purified by precipitation with alcohol, which, however, weakens it (Kjeldahl). Yeast is exhausted with alcohol, then carefully pounded with water and fine sand, and the invertase precipitated from the filtered solution by alcohol (Mayer).

Constitution.—Most of the authorities (except Gunning and Béchamp) agree that it is not an albuminoïd. Hartley concludes from the absorption spectra that invertase and diastase are very different from albumin, caseïn, and serin. Two analyses have been published, but no proof of the purity of the substances analysed is given.

Barth .... $C = 43·9$ $H = 8·4$ $N = 6·0$ $S = 0·63$
Donath ... $C = 40·5$ $H = 6·6$ $N = 9·4$

Barth's preparation also contained 22 per cent. of ash, which was allowed for in the calculations.

Properties.—As precipitated by alcohol, it is when dry a white substance, soluble in water yielding a neutral solution. It precipitates lead, copper, and mercurous salts, but has no action on iron perchloride or potassium ferrocyanide, and it is not rendered turbid on boiling with acetic acid (Barth). It is without action on starch, dextrin (Donath), maltose, dextrose, lævulose, inulin, and gum (Kjeldahl). It is considered by Béchamp to have an optical activity $[\alpha]_j = +41^{\circ}$. For the action on cane-sugar, the most favourable temperature is 50—60°, and the most favourable degree of concentration of the sugar solution 2—20 per cent. (Kjeldahl, Müller). Until 40 per cent. of the sugar is inverted, the transformation is proportionate to the time (Kjeldahl); but the products of inversion are strongly opposed to the reaction (Müller). The amount of inversion is not proportionate in any way to the amount of invertase present, and the time reaction does not follow the course of catalytic actions (Tamman). Invertase is not destroyed by its own action (Mayer), and it will invert about 750 times its own weight of sugar in 48 hours (Barth). The action is much hindered by alkalis and mercury salts, whilst acids in very small quantities augment it, hinder it in larger, and again augment it in still larger quantities; this last is, however, due to the inverting action of the acid itself (Kjeldahl).

Anthozymase.—Béchamp (*Mém. Acad. Sci.*, **28**, 347) claims to have isolated from the petals of *Robinia pseudoacacia* a ferment which he calls anthozymase, and which he says not only inverts cane-sugar but also saccharifies starch.

This substance is, like invertase, soluble in water and insoluble in alcohol. Its solutions are coagulated by heat. It has an optical activity $[\alpha]_j = -38°$ (*circa*). He was only able to obtain it in extremely minute quantities.

M. Béchamp adduces no evidence whatever to show that this is not an imperfectly purified mixture of diastase and invertase.

These are the principal published facts with regard to invertase; and we have given them in this form to avoid any necessity of again referring to them in the body of the article; what we add to the knowledge will be clear to anyone who wishes to study the subject, and we shall put forward what we consider new and important in the summary at the end.

Mode of Procedure.

We have already stated that the two great questions we wished to solve by this work were, first, the nature of the inverting power or function of invertase; and, secondly, the chemical composition of the active agent. The function of invertase is to transform sucrose according to the equation—

$$\underset{\text{Sucrose.}}{C_{12}H_{22}O_{11}} + H_2O = \underset{\text{Dextrose.}}{C_6H_{12}O_6} + \underset{\text{Lævulose.}}{C_6H_{12}O_6}.$$

Our first object was to determine if by the aid of what we could learn from the above-mentioned publications, and by any further experiments that might suggest themselves to us, we could find some quantitative expression for this function. We have so far no other factor which acts as a criterion of the purity of the substance, and no means of estimating it. We merely know that invertase is the only known substance which transforms cane-sugar, as described above, in the cold. We have no characteristic to guide us but this. Hence, when we have found that a certain product possessed this function, we have considered that invertase was present, whilst, on the contrary, if it did not invert cane-sugar under suitable conditions, we always considered that invertase was absent. From this it will be seen that we discarded the idea of such a substance as *dead* invertase. If a solution which was formerly known to contain invertase was found, under suitable circumstances, to have no power of inverting sucrose, we concluded that invertase was no longer present, and that the chemical substance, invertase, had been in some manner changed into another compound, or compounds.

It was clear at starting that we had to establish a method of estimating a *function* and not a quantity, or rather we had to find a quantitative expression for a function.

For this purpose it was necessary to make a choice between two theories for a working hypothesis. If Roberts is right, it is obviously of no use for our purpose to estimate the strength of such a variable quantity as the unspent vital force. If, on the contrary, the chemical theory is correct, it is without doubt possible not only to prove the presence or absence of invertase, but also its relative amount.

Once the laws which govern the reaction properly understood, it would, by estimating the intensity of the function, or, in other words, the extent or speed of the reaction, be easy to calculate *relatively* the amount of invertase present, just as we might estimate the amount of free sulphuric acid by its action on a boiling solution of sucrose under standard conditions. And invertase has one great advantage over sulphuric acid, in that there is no other known substance that acts in the same manner, and therefore we are not misled by the presence of other inverting agents.

This necessitated a complete study of the action of invertase on sucrose.

Before describing our experiments, it is as well that we should draw attention to some of the general laws relating to the course of chemical change. For this purpose we have made the following extracts from A. Vernon Harcourt's paper "On the Observation of the Course of Chemical Change" (*Journ. Chem. Soc.*, **20**, 460—492). They refer to an experiment entitled "On the Reaction of Hydrogen Dioxide and Hydrogen Iodide." In this reaction the amount of hydrogen iodide is kept constant by means of an excess of sodium hyposulphite, whilst the hydrogen dioxide is of course constantly decreasing in amount by being converted into water.

The following extracts give his chief results:—

"This result probably represents a general law of chemistry, which may be thus stated: When any substance is undergoing a chemical change, of which no condition varies excepting the diminution of the changing substance, the amount of change occurring at any moment is directly proportional to the quantity of the substance. . . .

"If the course of the change observed has been determined by a single gradual reaction, and the law of proportionality holds good, we shall expect to find that the amount of change at any moment has varied directly with the quantity of dioxide in the solution; and, if this be the case, the quantities of dioxide at the end of a series of times taken in arithmetical progression will be in geometrical progression, and the curve, as before, a logarithmic curve. . . .

"The amount of chemical change occurring at any moment is proportionate to the amount of dioxide in the solution.

"We have made a large number of similar sets of experiments under very various conditions. . . . Under all these circumstances the reaction still conforms to the same law. . . .

"The amount of chemical change occurring in the solutions at any moment varies directly with the amount of iodide, if all the other conditions are the same. . . .

"The amount of change varies directly (1) with the amount of dioxide, and (2) with the amount of iodide in a unit volume of the solution; (3) with the time during which the change proceeds; (4) with the total volume of the solution; and, finally, with some function of each of the other conditions under which the change occurs. Of these other conditions the quantities of hydrogen sulphate . . . and the temperature of the solution have been made the subject of experiment. . . .

"On comparing the rates at which the change proceeds with successive increments of acid, we find that these rates are in arithmetical progression. . . .

"The effect of varying the one essential condition of the change still remaining, namely, the temperature of the solution . . . appears to be of this kind. If a be the rate of change in any mixture at 0° C., the rate at any other temperature, say at h degrees, is ak^h. The value of k is about 1·07; whence it happens, conveniently for the memory, that for every 10° C. the rate of change is doubled."

The above are Harcourt's principal conclusions. They are supplemented by Esson (*Phil. Trans.*, 1867, pp. 123 *et seq.*), who shows that the equation applicable to a reaction proceeding according to the above laws is—

$$y' = ye^{-a(t'-t)},$$

when y and y' are the amounts of changing substance present in the solution at the beginning and end of an interval $t' - t$; a, the fraction disappearing in a unit of time; and e the base of the Napierian logarithms. This equation may be written in the form more convenient for calculation—

$$\text{Log}\log\frac{y}{y'} - \log(t' - t) = \log a + \log\log e.$$

Each separate observation supplies a value for log a + log log e, and these values should be identical.

In giving a quantitative expression to the function of invertase, we have not found it necessary to use this equation. Having once mapped out a theoretical curve on square paper, sufficient accuracy for our purpose was obtained by the quicker process of referring all future observations to it in the manner described under the heading "Estimation of the Strength of Invertase."

It may be convenient here to describe the methods and apparatus we employed. In performing experiments connected with the action of invertase on cane-sugar, the latter was first dissolved in boiling water and the solution allowed to cool. If the presence of sulphuric acid was required, the requisite amount was now added in the form of a decinormal solution (1 c.c. = 0·008 gram SO_3), and the solution was made up to the required bulk at 15·5°, space being left for the invertase-containing preparation. It was then placed in a water-bath automatically kept at the required temperature, and the vessel was covered over to prevent evaporation. The preparation under examination was now weighed or measured into a small beaker, and as soon as the temperature of the sugar solution was constant some of it was poured into the solution of invertase, and the whole poured back into the sugar solution. The small beaker was then rinsed with the solution and the time noted. The mixture was now left for inversion to proceed, and if at any time it was desirable to ascertain the progress of the reaction, it was accurately done as follows:—Into a small beaker was put half a drop of a very concentrated solution of potassium or sodium hydroxide. At a carefully noted time some of the solution was poured into this and well mixed with it. By this means the reaction was entirely stopped, and the sample could be examined at leisure; but we found it necessary, for reasons we shall presently give, to allow it to stand a quarter of an hour before doing so.*

When we desired to stop an inversion, it was done by adding sufficient alkali to give a reaction with litmus.

In order to ascertain the progress of inversion in the stopped solutions, they were examined at a temperature of 15·5°, by means of a Soleil-Ventzke-Scheibler polarimeter, and the result was recorded in the form:—100 mm. of the solution yields so many divisions, + or —, of the polarimeter scale. In order to save calculations, we always worked with these divisions, but they may be converted into degrees of $[\alpha]_j$ by multiplying by 0·384. It was generally necessary to calculate from the number of divisions observed the actual percentage of cane-sugar that had undergone inversion, and as the strength of the sucrose solution used was nearly always at the rate of 20 grams sucrose per 100 c.c. of solution, we used the following formula:—

---

* We may note here that we have only lately been acquainted with the necessity for this delay, and no doubt many of the minor irregularities in our results may be accounted for by not having regard to it.

$$(38{\cdot}4 - d) \div 0{\cdot}518 = p.$$

d = divisions of polarimeter scale given by 100 mm. of the solution.
p = per cent. of cane-sugar inverted.

38·4 is the number of divisions corresponding to the original sucrose solution, and 51·8 is the total number of divisions that the polarimeter reading would fall through if the sugar were all inverted.

These figures are equal to an optical activity for cane-sugar $[\alpha]_j = +73{\cdot}8°$, for dextrose $[\alpha]_j = +57°$, and for levulose $[\alpha]_j = -106°$.

In dealing with solid invertase preparations we have, for the purpose of drying them perfectly, always used a water-bath, so constructed as to admit a constant stream of well-dried air at a temperature of 100° to circulate over the powdered substance, thus causing rapid and perfect elimination of water even in very hygroscopic preparations.

The estimations of nitrogen were all done by combustion with copper oxide, and the carbon and hydrogen determinations by combustion in oxygen. The estimation of the optical activity of the purified substances was, whenever possible, performed by drying the powder in the water-bath until constant, then dissolving in a weighed quantity of water, and taking, first, the specific gravity, and then the optical activity of the solution. The divisor, D, was calculated from this by the formula—

$$\frac{G - 1000}{W} = D.$$

G = the specific gravity of the solution, taking water at 1000.
W = grams of the substance per 100 c.c. of the solution.

We shall now proceed to describe in detail the results we have obtained in examining the action of invertase on cane-sugar, and to compare them carefully with what we should expect if the reaction followed the laws we have quoted. We shall at the same time state any other facts of interest which we have come across, in the hope that we may be able to throw some light on the chemistry of the action.

PART II.—THE ACTION OF INVERTASE ON CANE-SUGAR.

Rapidity of the Reaction.

It is well known that the action of invertase is much more rapid at the beginning of the reaction than at the end; but the exact curve which the reaction follows has not hitherto been mapped out. We find that whatever the conditions under which an inversion takes place, as long as these conditions remain unaltered the reaction proceeds on a definite and regular curve, and, the speed of the reaction being once established by means of two separate observations, we can predict the course of the whole of the rest of the reaction. An alteration of the conditions under which the reaction takes place simply alters its speed, but, if allowance is made for this altered pace, the reaction follows the original curve.

In Plate I (p. 844) are shown the results of three carefully conducted experiments, undertaken to establish this curve. The vertical lines indicate time-units (that is to say, equal time intervals), whilst the horizontal ones show the percentage of the total sucrose that has been inverted. The three experiments were made at different temperatures and with different proportions of the same preparation of invertase. We have also made other experiments with very different degrees of concentration of the sugar solution and varying conditions of acidity, &c., but we have always found the inversion to follow a curve similar to the ones here plotted; we only publish these three as being those most carefully performed. The plain line in the plate shows the course a reaction would take if it followed the law laid down by Harcourt for a reaction in which the only varying condition is the diminution of the changing substance.

In plotting the theoretical curve, we have taken it that 10 per cent. of the total of the changing substance was changed in the first of the time-units (or "T"). Then, according to the above law, 10 per cent. of the remainder of the changing substance would be changed in the second time-unit (or T). As the changing substance would be only 90 per cent. of the whole original amount, this means that in the second T 9 per cent. would be changed. In the third T there would be only 81 per cent. to act upon, so that only 8·1 per cent. would be changed during this time-unit, leaving only 72·9 per cent. of changing substance for the reagent to act upon in the fourth T. By this mode of calculation, a theoretical completion of the reaction is never reached: at the conclusion of 44 time-units we still find 1 per cent. of the original changing substance left.

The following are the details of the three experiments on the inversion of cane-sugar above alluded to; the results are plotted, side by side, with the theoretical curve on the Plate.

Experiment A.—Temperature 15·5°. 100 grams of cane-sugar, 4 c.c. decinormal sulphuric acid, and 2 grams of the solution of invertase preparation were mixed and made up to 500 c.c. In order to compare the course of the action with the theoretical curve plotted as above described, it was necessary to make the two curves correspond at two points of their course. For these we have chosen the starting point and the point of no optical activity. The theoretical line crosses the point of no optical activity at 12·7 time-units. In the experiment the inversion took 180 minutes to reach that point.

$$\frac{180}{12\cdot7} = 14\cdot17 = \text{the value in minutes of 1 T.}$$

In Plate I the points of observation are surrounded by small circles, marked "A," and they are connected by a line of dashes.

In Table I, the details of the experiment are given. The third column gives the number of time-units which have elapsed since the start. It is obtained by dividing the observed minutes by 14·17.

The percentage of sucrose inverted is calculated by the formula already given.

TABLE I.—*Rapidity of Inversion at* 15·5°.

Time.	Minutes from start.	T.	Reading in 200 mm. tube.	P. c. inverted.
*8.36 A.M.	start	0	—	0
8.41 ,,	5	0·35	+73·6	3·1
8.51 ,,	15	1·06	+66·6	9·8
*9.6 ,,	30	2·12	+56·9	19·2
*9.33 ,,	57	4·01	+42·0	33·6
10.6 ,,	90	6·36	+27·4	45·8
*10.36 ,,	120	8·47	+16·2	58·5
11.6 ,,	150	10·59	+ 7·0	67·4
11.38 ,,	182	12·84	− 0·4	74·5
*12.6 P.M.	210	14·83	− 5·9	79·8
12.36 ,,	240	16·95	−10·7	84·4
1.6 ,,	270	19·05	−13·7	87·3
*2.57 ,,	381	26·89	−20·1	93·5
3.46 ,,	430	30·35	−21·7	95·1
5.4 ,,	508	35·85	−23·0	96·3
*9.6 A.M.	1470	103·7	−26·0	99·2
48 hours	—	—	−26·9	100·0

Experiment B.—Temperature 35·5°. 1 c.c. of decinormal sulphuric acid, and 1 gram of the invertase solution. The other conditions are the same as in Experiment A. The value of T was found to be

Journ. Chem. Soc. Oct 1890

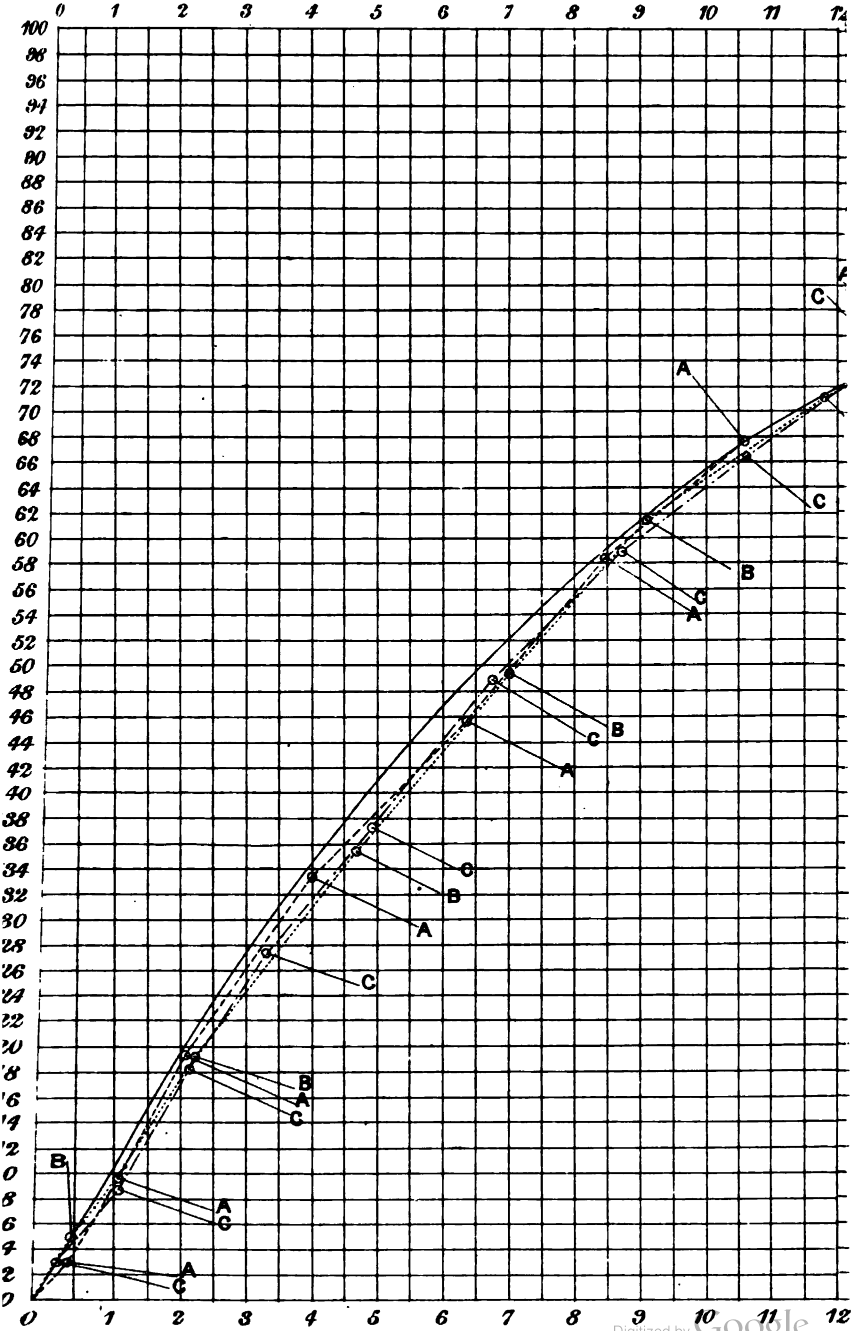
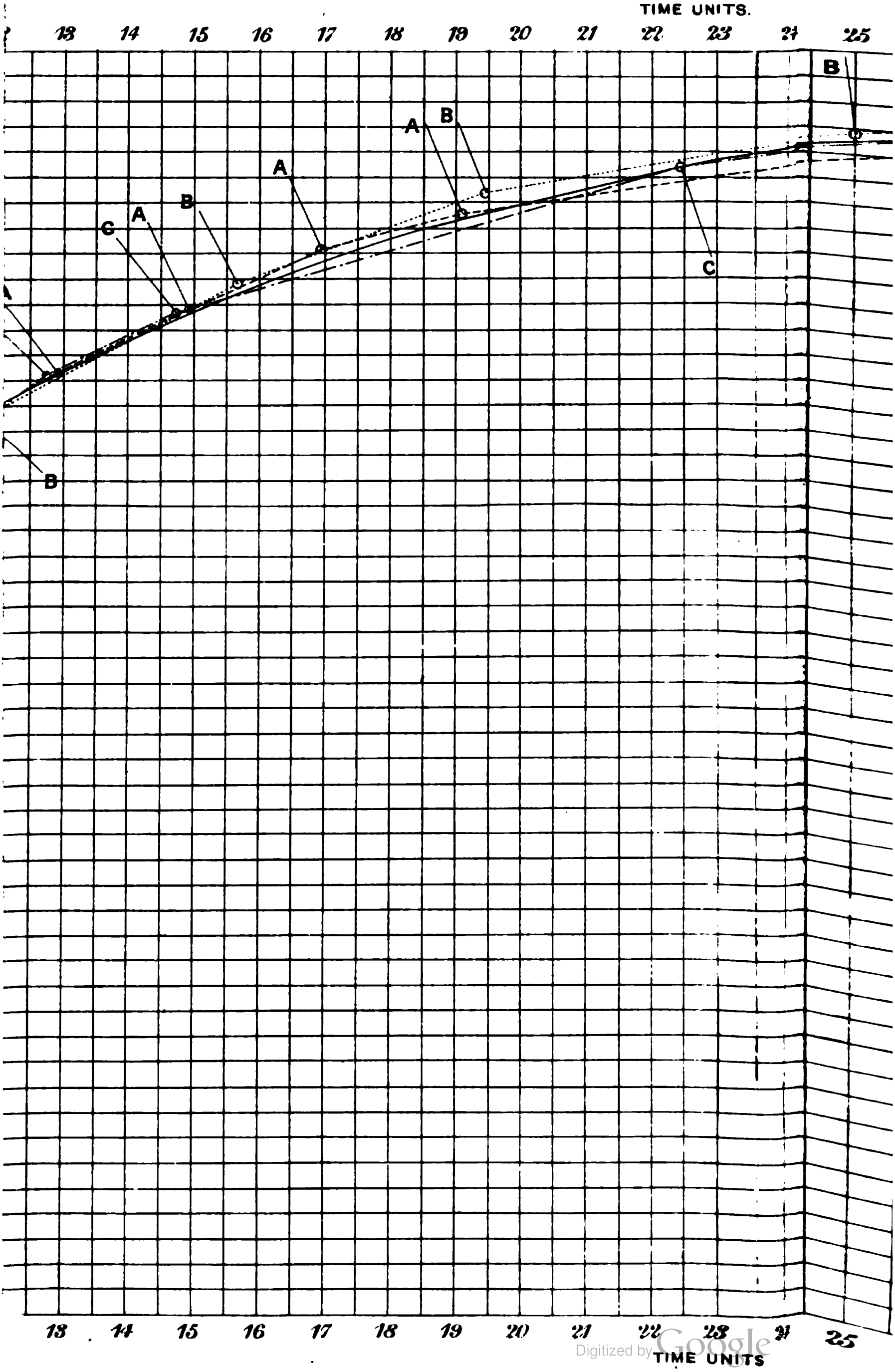
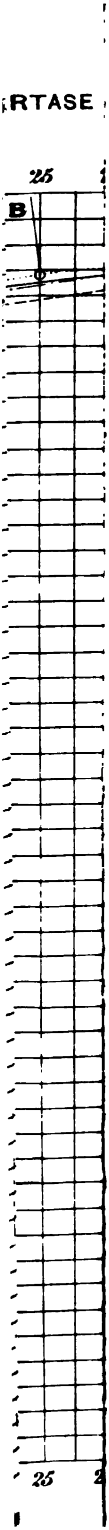


PLATE I. THE TIME CURVE OF THE ACTION OF INERTAS





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43 minutes. In the Plate the points of observation are marked "B," nd are connected by a line of dots.

TABLE II.—*Rapidity of Inversion at* 35·5°.

Time.	Minutes from start.	T.	Reading in 200 mm. tube.	P. c. inverted.
*9.31 A.M.	start	0	—	0
9.35 ,,	4	0·47	+71·7	4·9
*9.50 ,,	19	2·25	+56·9	19·2
*10.10 ,,	39	4·63	+40·2	35·3
10.30 ,,	59	7·00	+25·5	49·5
*10.50 ,,	79	9·16	+12·8	61·8
11.10 ,,	99	11·74	+ 3·3	71·0
*11.43 ,,	132	15·66	− 8·0	81·9
12.15 P.M.	164	19·45	−15·1	88·7
*1.2 ,,	211	25·03	−20·4	93·8
3.50 ,,	379	44·96	−24·5	97·8
*5.31 ,,	480	56·94	−26·2	99·4
24 hours	—	—	−26·9	100·0

Experiment C.—Temperature 54°. 0·25 c.c. decinormal sulphuric acid, and 0·25 gram invertase solution. The other conditions are the same as in Experiments A and B. The value of T was found to be 16 minutes. In the Plate, the points of observation are marked "C," and are connected by a line of alternate dots and dashes.

TABLE III.—*Rapidity of Inversion at* 54°.

Time.	Minutes from start.	T.	Reading in 200 mm. tube.	P. c. inverted.
*9.4 A.M.	start	0	—	0
9.9 ,,	5	0·31	+73·6	3·1
*9.21 ,,	17	1·06	+67·7	8·8
*9.39 ,,	35	2·19	+57·8	18·3
9.59 ,,	55	3·44	+48·1	27·7
*10.22 ,,	78	4·88	+38·2	37·3
10.52 ,,	108	6·75	+26·0	49·0
*11.23 ,,	139	8·69	+15·5	59·2
11.54 ,,	170	10·63	+ 7·7	66·7
12.28 P.M.	204	12·75	− 0·2	74·3
*12.59 ,,	235	14·69	− 5·7	79·6
*3.3 ,,	359	22·44	−17·3	90·8
5.1 ,,	477	29·81	−23·1	96·4
*9.4 A.M.	1440	90·0	−24·0	97·3
48 hours	—	—	−26·8	100·0

From the Plate it will be seen that the curves founded on these three experiments follow the line of the above-quoted law with great closeness. Considering the nature of the experiments, the deviations are far within the limits of errors of manipulation. It must be remembered that the slightest alteration in the temperature causes considerable variation in the speed of the reaction. There are also other sources of error connected with the taking and the killing of the samples, and, towards the end of the reactions, errors due to the want of absolute accuracy in the sugar solution and to the optical activity of the inverting preparation are sufficient to account for very considerable discrepancies. We maintain, therefore, that taking the individual experiments the deviations are considerably less than those which might reasonably be expected, and the evidence is so far conclusive that the reaction follows the law we have enunciated. But if we look more closely at the diagram, we see that the deviations from the theoretical line, though small in themselves, are constant in the three experiments; in fact they correspond in a very striking manner. This might possibly be accidental for three experiments only, but we find that the curves of many other reactions that we have followed deviate from the theory in a similar manner.

A careful analysis of Tables I, II, and III will give the different rates of the reaction at different points of its progress. We have taken the observations marked with an asterisk in these tables, and have calculated the speed of the reaction between every two of them. Then, taking it for granted that the rest of the reaction proceeds on the theoretical curve, we have, from this rate of progress, calculated the time required to reach the point of no optical activity. For purposes of comparison between the three experiments, we have assumed the average speed of each reaction to this point to be 100 minutes, and we have thus obtained a series of numbers which are strictly comparable among themselves. If the reactions followed the theory exactly, the figures would all be 100·0; and, as the figures represent minutes, the higher the figure, the slower the reaction—in simple proportion.

Table IV.—*Rapidity of the Reaction at Different Points compared with the Theoretical Reaction.*

Per cent. inverted.	A Expt.	B Expt.	C Expt.	Average.
	minutes.	minutes.	minutes.	minutes.
0—20	105·9	112·7	112·2	110·3
20—35	102·1	110·3	107·5	106·6
35—60	96·7	94·9	93·0	94·9
60—80	96·2	88·6	92·3	92·4
80—93	83·2	103·0	105·6	97·3
93—99	275·5	104·1	496·8	292·1

These figures all show a continuous increase in activity up to a certain point, about 80 per cent. of inversion, and after that a large and increasing decrease. The figures themselves are of course not very accurate; the intervals between the observations are too small to permit this, and in the case of those in the last line, 93—99 per cent. inverted, the difference between the optical activities is too small, and the accidental errors are too great to admit of high accuracy; still the numbers agree wonderfully among themselves, and, as we have said before, we have done many other inversions, and all of them point to similar results.

In conclusion, we repeat that the reaction may be considered to follow a curve similar to that obtained from a reaction following Harcourt's law, but that, owing to some slight modifying circumstance, which we cannot explain, the reaction, compared with the theoretical curve, keeps increasing in rapidity until about 80 per cent. of inversion is reached, when it begins to get slower in comparison with the curve, and ultimately, just before the completion of the reaction, it gets very much slower than it should do if it adhered to the law.

Influence of the Proportion of Invertase Present.

We experienced great difficulty in discovering any relationship between the proportion of invertase preparation employed and the work done by it. For a long time we got the most incoherent results. At last, after hundreds of experiments, we found that it is absolutely necessary, in order to get comparable results, that the acidity of the solution should be such that it is in the most *favourable condition* for the action of invertase. This degree of acidity varies with every variation of the conditions under which the reaction takes place, and details of our experiments on this point will be found under heading, "Influence of Foreign Substances." Now, granted that the acidity is in the most favourable proportion, we find a very simple rule holds good, namely:—The time necessary to reach any given percentage of inversion is in inverse proportion to the amount of the inverting preparation present, and, therefore, to the amount of the invertase; that is to say, the time is in inverse proportion to the inverting agent.

In Table V we give details of two series of experiments made with the object of establishing this law. 10 grams of sugar were dissolved in 50 c.c. of water for each experiment. The most favourable degree of acidity was in each case determined beforehand; but as this most important factor varies a little with every different sugar solution, it is probable it was a source of error.

TABLE V.—*Rapidity of Inversion with Varying Proportions of Invertase Preparation.*

Exp.	Temp.	Invertase preparation. Grams.	SO_2, parts per 100,000.	Times of		Reading in 200 mm. tube.	Minutes to point of no optical activity.	
				Start.	Stopping.		A.	B.
1	15·5	0·15	7·5	11.40	4.41	− 2·0	283·0	424·5
2	15·5	0·45	12·5	3.0	4.40	− 1·8	94·8	426·6
3	15·5	1·50	20·0	11.56	12.26	+ 1·0	30·7	460·5
4	56·5	0·0345	1·0	11.0	12.43	+16·5	157·6	54·4
5	56·5	0·0722	1·5	11.22	12.15	+13·5	74·8	54·0

In the column marked "A" we give the time necessary for the reactions to reach the point of no optical activity, and in column "B" the time that would have been necessary to reach this point if 0·1 gram of the invertase preparation had been employed—assuming that the time is in inverse proportion to the inverting agent.

The method of calculation is as follows:—

From the polarimeter reading we calculate by the formula already given the percentage of sucrose that was inverted. This factor we refer to the theoretical time curve in the Plate, and note the number of time-units (T) to which it corresponds. Now, when a solution of sucrose has no optical activity, it is shown by the formula to be inverted to the extent of 74·1 per cent., and this number will be seen to correspond on our theoretical time curve to 12·7 T. We can now easily calculate the time when the reaction would arrive at 12·7 T by simple proportion; and this number we give in column A.

As an example of the method of calculation we will take Experiment 1. The percentage of inversion calculated by the formula is 76·1; and if we refer this to the Plate, we shall see that it corresponds to 13·5 T. The number of minutes required to reach this was 301.

$$13{\cdot}5 : 12{\cdot}7 :: 301 : 283.$$

This last is the number of minutes the reaction took to arrive at the point of no optical activity.

In order to find out how long the reaction would have taken to reach this point if only 0·1 gram of the invertase preparation had been used, we have, if our law is correct, only to multiply the number already obtained by the grams of invertase preparation employed and then divide by 0·1. We thus get the number 424·5, which we give in column B.

As the same invertase preparation and the same temperature were employed throughout each series, we should find, if our law is correct, that in each series the figures given in column B are identical. This is substantially the case with the exception of Exp. 3, which differs from Exps. 1 and 2 to the extent of about 7·5 per cent. In experiments of this kind this may be considered to be almost within the errors of manipulation; but in this case we believe it to be due to an insufficient amount of acidity.

Further confirmation of this law will be found in Tables X—XV, the results of which are plotted out in Plates III and IV (pp. 856, 858). In these diagrams it will be seen that at the most favourable degree of acidity the curves attain approximately the same height. In each case the curve produced from the smallest amount of invertase comes between the other two, and in one case the greatest amount of invertase is at the top, and in the other case at the bottom. Under these circumstances we can only suppose that these are errors of manipulation, and conclude that we have proved the law:—The time necessary to reach any given percentage of inversion in a solution containing the amount of acid most favourable for the action of invertase is in inverse proportion to the amount of invertase present.

This result is in exact accord with the results of Harcourt's investigations on the Laws Regulating Chemical Change.

Influence of the Concentration of the Solution.

The following table shows some results obtained by varying the amount of water present, all other conditions remaining the same.

The temperature was 54°, and the raw material (yeast) was used as the inverting agent.

TABLE VI.—*Rapidity of the Reaction with Varying Concentration of the Solution.*

Cane-sugar. Grams per 100 c.c.	Yeast. Grams per 100 c.c.	Times of		Reading in 100 mm. tube.	Minutes to point of no optical activity.
		Start.	Stopping.		
15	0·15	10.37	12.27	+12·5	274
20	0·20	10.38	12.28	+11·0	194
25	0·25	10.39	12.29	+14·0	200
30	0·30	10.40	12.30	+18·8	215
40	0·80	10.56	12.53	+ 6·4	278*
50	1·00	10.56	12.53	+23·8	386*

* In these numbers the increased proportion of yeast to sugar has been allowed for.

In calculating these results, we have proceeded generally in the same manner as in Table V. In the first four experiments the proportion of yeast was 1 per cent. on the weight of sucrose, so the results were directly comparable; but in the last two experiments the yeast was raised to 2 per cent. on the sugar, so, in obedience to the law proved under the last heading, it was necessary to divide the minutes by 2 before comparing with the former numbers.

From these results it will be seen that about 20 grams of cane-sugar per 100 c.c., or probably a little more, is the most favourable degree of concentration for inversion. More dilute solutions are very unfavourable to the reaction, whereas concentration greater than 20 grams is only slightly detrimental until 40 grams to the 100 c.c. is reached.

These remarks, of course, only apply to a temperature of 54°.

Harcourt gives no separate rule for the effect of varying the amount of the solvent, but it is no doubt included in the statement that the amount of change varies directly "with some function of each of the other conditions under which the change occurs."

It is evident from the results we have given that this is not the case with this reaction; and we believe the reason to be that the conditions under which the experiments were conducted were not in this respect comparable. Harcourt's experiments were conducted with comparatively dilute inorganic solutions, ours with very strong and, to some extent, viscous solutions.

In his experiments the increase of viscosity obtained by decreasing the amount of the solvent would be trifling, and would not, practically, affect his results. In our experiments, on the contrary, every decrease in the amount of the solvent affects very seriously the fluidity of the solution, and hence, no doubt, impedes chemical action. If the concentration is low, the increase in viscosity is trifling, and not nearly sufficient to counteract the stimulative effect of the increase of concentration. The effect of the viscosity increases rapidly as the concentration increases, and at about 20 per cent. the two are balanced. Beyond that point the effect of the viscosity becomes greater and greater until in the case of a saturated solution of cane-sugar the viscosity is so great that invertase only acts with extreme slowness. We think in this manner our results are satisfactorily accounted for without coming into conflict with Harcourt's observations.

Influence of Temperature.

We made some experiments with a view to determining the comparative rate of inversion at different temperatures. In Table VII we give the results obtained from the solutions which contained proximately the most favourable amount of acid. Some experi- ents were done at 60°, but the influence of the minutest traces acid was so excessive that we did not pursue these experiments. he number given for 60° must therefore be taken as very doubtful; is will be seen from the full results given under the heading Influences of Foreign Substances." It is there shown that though he experiments were conducted at intervals of one-half part of acid er million of solution, this degree of accuracy was not nearly ufficiently great.

At each temperature we made three or more experiments with slightly ifferent amounts of acidity. Several complete series are given in Tables IX and XVI. In Table VII we have, however, only given the one which yielded the most favourable results. Each experiment was performed with 10 grams sucrose dissolved to 50 c.c. The same sugar solution and the same invertase preparation were used throughout.

TABLE VII.—*The Influence of Temperature on the Rapidity of Inversion.*

Nos.	Temperature.	Invertase preparation. Grams.	SO_3 parts per 100,000.	Times of		Reading in 200 mm. tube.	Minutes to point of no optical activity calculated for 0·1 gram invertase preparation.
				Start.	Stopping.		
1	0·0	0·6	15·0	10.56	2.33	+8·8	1440·0
2	15·5	0·18	4·0	11.16	2.29	+5·0	398·0
3	29·5	0·05	1·0	11.45	5.4	−1·0	155·5
4	45·0	0·051	0·6	10.37	12.39	+6·3	73·8
5	55·0	0·033	0·6	10.27	1.34	−6·0	51·8
6	60·0	0·0342	0·5	11.38	3.22	+1·8	80·4

The calculations were the same as in previous cases; the variants, other than temperature, which were necessitated by the requirements of the experiments, being allowed for in accordance with the facts already described. Hence the numbers given in the last column represent proportionately the activity of the inverting preparation at the various temperatures.

In order to compare these results with Harcourt's law, we refer to Plate II (p. 852), in which the horizontal lines represent temperature, and the vertical ones time. The places where the observations fall are marked with small circles, and they are joined by a dotted line.

We have denoted by a continuous line the course the reaction should take if it followed Harcourt's law, that for every 10° increase of temperature the rate of change is doubled.

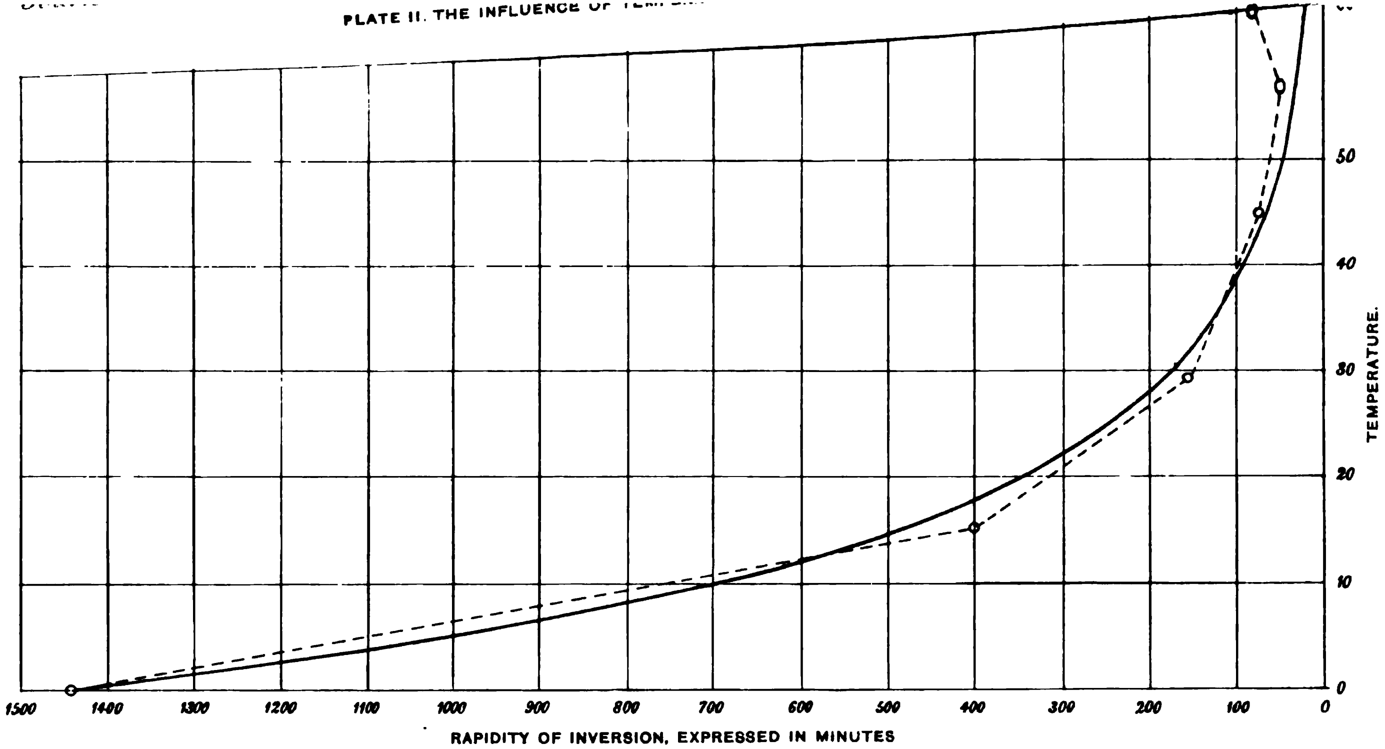
A comparison of these two curves shows us that they do not absolutely agree. At lower temperatures, the differences are in fact, comparatively, so small for experiments of this sort that we think ourselves justified in saying that the reaction is, in this respect, in accord with Harcourt's law. At higher temperatures there is, however, a decided falling off from the rate indicated by the curve. According to this law invertase should be 16 times as strong at 55·5° as at 15·5°, whereas we found it to be only 7·5 times as active. We should like, however, to point out that we have not seen any record of experiments made at a temperature so high that it approaches the point where the reaction would cease. Possibly, under these circumstances, the results obtained would be in accord with those here noted.

We have made some experiments showing that invertase in solution, heated to a temperature of 60° in the presence of an excess of cane-sugar, is not permanently affected. Some results which clearly show this will be given when we come to Table XXXI. This is an important point, as it shows that the effect that temperatures under 60° have on a solution undergoing inversion is limited to the time the temperature lasts. To make this more clear, we will suppose that a certain inversion is proceeding at a rate which would be expressed by the formula $\pm 0 = 100'$, the temperature being 15·5°. If the temperature is now raised to 60°, the rate of inversion would be greatly increased, and for the time it remains at 60° the rapidity might perhaps be expressed by $\pm 0 = 15'$. If now the temperature is again lowered to 15·5°, the inversion will again proceed at that temperature at its former rate, $\pm 0 = 100'$.

Influence of Foreign Substances.

The Action of Alkalis.—The caustic alkalis, even in very small proportions, are instantly and irretrievably fatal to the reaction, and the hydrates of the alkaline earths are extremely detrimental to it. It is a remarkable fact that if an inversion is stopped with a little alkali only—sufficient to render good test-paper distinctly blue, and the solution at once observed through a polarimeter, it will be seen that the angle continues to decrease for some considerable further time. This looks as if the amount of alkali was not sufficient to kill the invertase instantly, but required time to do it. That this is not so is proved by the fact that if a second sample is taken at the time of "stopping," and stopped with a large excess of alkali, it does not show any slow residual movement downwards, but at once assumes the angle that the slightly alkaline solution eventually attains to.

PLATE II. THE INFLUENCE OF



HARRISON & SONS LITH. ST MARTINS LANE W C

We give an example of this in the following experiment. A solution of cane-sugar was mixed with a large amount of invertase solution. After allowing the reaction to proceed for a quarter of an hour, two small samples (about 20 c.c.) were taken and simultaneously stopped, A with one-fourth of a drop of very strong potash solution, and B with 4 drops. They were both quickly examined in the polarimeter with the result that B at once showed an angle = +32·2, which fell after 18 hours standing to 30·8; whilst A started at +39, and kept slowly descending for a long time, eventually reaching +29·8.

The following are the readings from A sample:—

Time.	Reading.	Time.	Reading.
4·0	stopped	4·23	+33·7
4·2	+39·0	4·35	+33·2
4·5	+36·6	4·55	+32·6
4·7	+36·0	5·25	+32·5
4·12	+34·3	after 18 hours	+29·8

We see from this that the small amount of alkali must have killed the invertase just as quickly as the larger one. It is also evident that in the case of the large amount of alkali there must have been a large jump down on rendering alkaline. We further proved this in the following experiments:—

A 20 per cent. solution of sugar was prepared and divided into two portions, A and B. To A, 5 per cent., and to B, 10 per cent. invertase solution was added. At intervals, polarimetric readings were made of each, and at the same instant, small samples of them were stopped by the addition of several drops of strong potash, and readings of these also made. The observations were made in a 200 mm. tube; the results are given in the following table:—

TABLE VIII.—*The Decrease of Optical Activity on stopping Inversion with Alkali.*

A Expt. 5 per cent. invertase solution.			B Expt. 10 per cent. invertase solution.		
Before stopping.	After stopping.	Decrease.	Before stopping.	After stopping.	Decrease.
+74·7	+70·3	4·4	—	—	—
+67·8	+58·5	9·3	—	—	—
—	—	—	+64·8	+49·0	15·8
+38·3	+21·0	17·3	—	—	—
—	—	—	+21·6	−2·5	24·1
+8·7	−7·0	15·7	—	—	—
—	—	—	−16·0	−24·2	8·2

The decrease of 24·1 divisions observed in B experiment is equivalent to the inversion of 23·3 per cent. of the total sucrose originally present.

We call this fall, after stopping, "the residual decrease."

Of course all the numbers given for the inverting process were obtained from observations taken after the residual decrease had taken place; we prove this method to be correct under the heading "Molecular Weight of a Solution of Cane-sugar undergoing Inversion." It is already clearly evident from the general agreement of our results, that the decrease is in no way due to any direct inverting action of the alkali. One law alone would prove that the whole of the inversion is due to the invertase; we refer to our numbers showing that the action of invertase is in proportion to its weight. We shall explain the cause of the residual decrease under the heading "Theory of Inversion by Invertase."

From these facts will be seen the necessity for allowing a stopped solution to stand a quarter of an hour before taking the final reading.

The action of acids is peculiar and complicated. Kjeldahl states, with perfect correctness, that in extremely minute quantities they greatly aid the reaction; but if these quantities are increased this action is reversed, and they are very detrimental. This is a most important matter, as without a knowledge of the action of dilute acids it is impossible to estimate the strength of invertase preparations.

In the following tables we give the effect of varying the amount of sulphuric acid present. In each experiment 10 grams of sugar was used, and the bulk of the total solution was 50 c.c. As most of these tables contain results from more than one series of experiments, they are not always absolutely regular, the proportion of acidity being so small that the most favourable point varies for each series. We have thought it best, however, to put in *all* the experiments, as they cover a wider range. In a single series we always find that the results are perfectly regular. In the column headed "Series" we have distinguished each series with a different letter. The sulphuric acid is expressed as SO_3 in parts per 100,000 on the total solution; a very dilute solution of it was made, and a measured quantity used. In the case of the invertase solution it was either measured, with or without dilution, or weighed, according to the amount wanted; its sp. gr. was 1·020; it was generally added to the sugar solution before subdividing into lots of 50 c.c.

The results are calculated in every way the same as those in Table VII.

TABLE IX.—*Influence of Sulphuric Acid on Rapidity of Inversion at 0°.*

Sugar, 10 grams. Invertase solution, 0·6 gram = 6 per cent. on the sugar. Total solution, 50 c.c. Temperature, 0°. In Plate III (p. 856) the curve is indicated by a line of crosses.

Experiment.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity calculated for 0·1 gram invertase preparation.
1	15	10.56	2.33	+ 3·8	1440
2	25	"	"	+ 4·9	1476
3	35	"	"	+ 8·0	1608
4	56	"	"	+25·6	2586

TABLE X.—*Influence of Sulphuric Acid on Rapidity of Inversion at 15·5°.*

Sugar, 10 grams. Invertase solution, 0·15 gram = 1·5 per cent. on sugar. Total solution, 50 c.c. Temperature, 15·5°. In Plate III the curve is indicated by a dotted line.

Experiment.	Series.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity calculated for 0·1 gram invertase preparation.	
1	A	none	10.43	3.15	+ 8·8	513	
2	A	2·5	"	"	+ 0·2	412	
3	A	5·0	"	"	− 1·0	396	396
4	D	5·0	12.27	5.5	− 1·9	395	
5	A	7·5	10.43	3.15	− 1·4	390	
6	A	10·0	10.43	3.15	− 1·3	391	391
7	B	10·0	10.33	3.20	− 3·7	386	
8	D	10·0	12.27	5.5	− 1·7	395	
9	B	20·0	10.33	3.20	+ 0·5	437	
10	B	30·0	"	"	+ 6·0	502	
11	B	50·0	"	"	+20·4	738	
12	B	150·0	"	"	+62·0	3640	
13	E	250·0	23 hours		+58·4	14000	

TABLE XI.—*Influence of Sulphuric Acid on Rapidity of Inversion at 15·5°.*

Sugar, 10 grams. Invertase solution, 0·45 gram = 4·5 per cent. on the sugar. Total solution, 50 c.c. Temperature, 15·5°. In Plate III the curve is indicated by a line of dashes; the first portions of it (up to 10 parts SO_3) and some of the latter portions are obtained from a different source, and need only be regarded as probable.

Experiment.	Series.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity calculated for 0·1 gram invertase preparation.
1	F	10	2.28	5.2	−15·6	415
2	F	15	2.28	5.1	−15·4	415
3	F	20	"	"	−14·6	430
4	F	250	"	"	+60·4	5453
5	F	500	"	"	+72·0	19950

TABLE XII.—*Influence of Sulphuric Acid on Rapidity of Inversion at* 15·5°.

Sugar, 10 grams. Invertase solution, 1·5 grams = 15 per cent. on the sugar. Total solution, 50 c.c. Temperature, 15·5°. In Plate III the curve is indicated by a line of alternate dots and dashes.

Experiment.	Series.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity calculated for 0·1 gram invertase preparation.	
1	H	none	3.24	3.49	+12·3	405	512
2	J	none	4.8	4.38	+16·5	542	
3	K	none	11.25	12.0	+13·7	590	
4	H	10	3.24	3.49	+ 8·6	368	374
5	J	10	4.8	4.38	+ 2·8	380	
6	H	20	3.24	3.49	+ 7·1	354	363
7	J	20	4.8	4.38	+ 2·1	372	
8	H	30	3.24	3.49	+ 7·5	357	352
9	J	30	4.8	4.38	+ 3·1	381	
10	K	30	11.26	12.0	− 7·4	319	
11	J	40	4.8	4.38	+ 3·6	381	
12	K	45	11.27	12.1	− 5·4	340	
13	J	50	4.8	4.38	+ 4·1	391	
14	J	60	4.8	4.38	+ 6·0	413	382
15	K	60	11.27	12.0	− 3·4	351	
16	J	120	4.8	4.38	+22·2	634	
17	K	250	11.28	12.0	+54·6	2090	

In Plate III we have mapped out the results given in Tables IX to XII.

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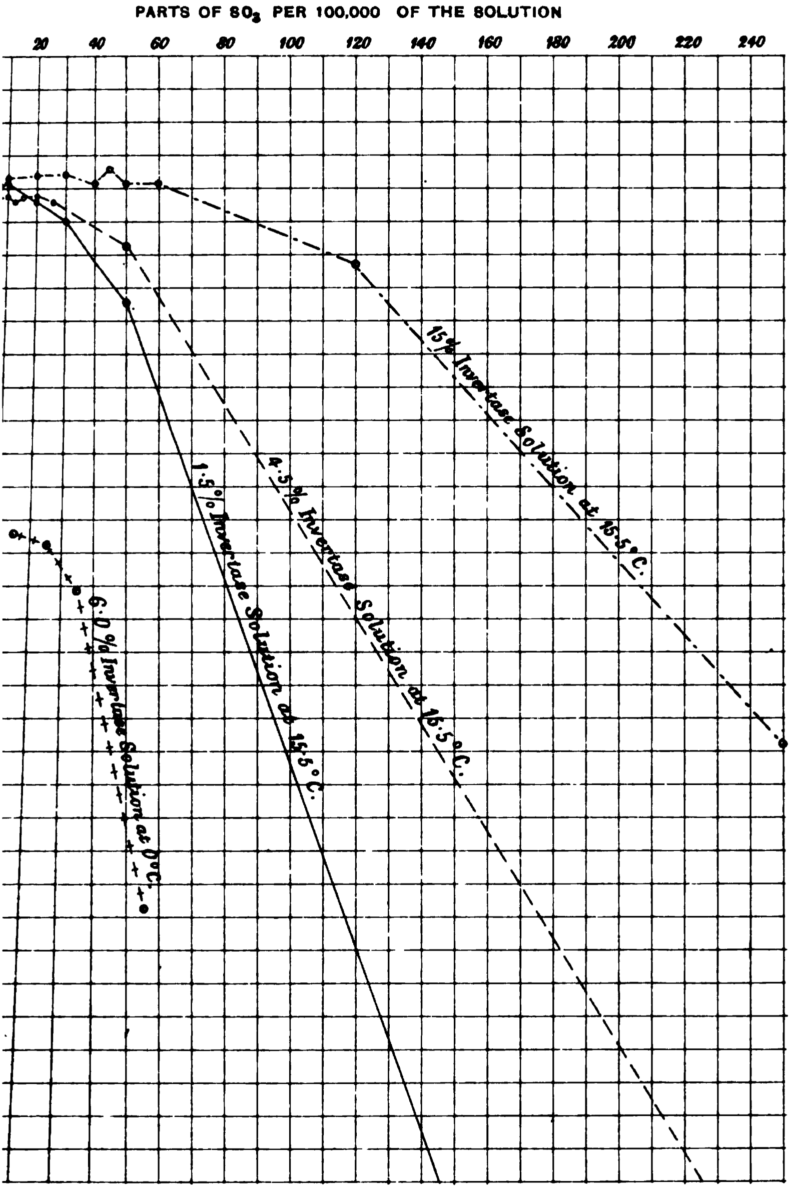
I. THE INFLUENCE OF SULPHURIC ACID ON RAPIDITY OF INVERSION AT 0° AND AT 15·5° C



HARRISON & SONS LITH. ST MARTINS LANE W.C

BLE XIII.—*Influence of Sulphuric Acid on Rapidity of Inversion at 56°.*

ugar, 10 grams. Invertase solution, about 0·04 gram = 0·4 per . on the sugar. Total solution, 50 c.c. Temperature, 56°. In te IV (p. 858) the curve is indicated by a dotted line.

eri-nt.	Series.	Invertase solution in grams.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity, calculated for 0·1 gram invertase preparation.
	Q	0·0355	none	10.51	12.37	+22·0	66·0
	O	0·04	0·5	12.43	3.27	− 9·6	48·4
	„	0·042	1·0	12.44	3.27½	−12·4	45·9
	„	0·04	1·5	12.45	3.27½	−10·6	46·5
	„	0·04	2·0	12.45	3.27	− 8·6	49·7
	Q	0·0367	6·0	11.14	1.1	+37·0	108·4

BLE XIV.—*Influence of Sulphuric Acid on Rapidity of Inversion at 56°.*

ugar, 10 grams. Invertase solution, 0·07 gram = 0·7 per cent. the sugar. Total solution, 50 c.c. Temperature, 56°. In Plate IV curve is indicated by a line of dashes.

eri-nt.	Series.	Invertase solution in grams.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity, calculated for 0·1 gram invertase preparation.	
	R	0·07	none	11.19	12.52	+10·0	84·3	
	N	„	0·5	3.49	4.58	+ 0·6	49·1	
	„	„	1·0	3.50½	4.58	− 2·6	44·0	
	„	„	1·5	3.52	4.58	− 1·6	44·3	
	„	„	2·0	3.53	4.58	0·0	45·5	44·8
	M	„	2·0	3.57	5.24	−10·4	44·0	
	„	„	3·0	„	„	− 8·0	47·7	48·7
	R	„	3·0	11.19	12.52	− 8·6	49·7	
	M	„	4·0	3.57	5.24	− 4·0	54·1	
	„	„	5·0	„	„	+ 4·6	68·4	
	R	„	9·0	11.19	12.52	+54·0	344·0	

TABLE XV.—*Influence of Sulphuric Acid on Rapidity of Inversion at 56°.*

Sugar, 10 grams. Invertase solution, about 0·15 gram = 1·5 per cent. on the sugar. Total solution, 50 c.c. Temperature, 56°. In Plate IV the curve is indicated by a line of alternate dots and dashes.

Experiment.	Series.	Invertase solution in grams.	SO_3 parts per 100,000	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity, calculated for 0·1 gram invertase preparation.
1	P	0·156	0·5	3.32½	4.7½	+1·0	54·8
2	"	0·153	1·0	3.36½	4.11½	−3·4	47·3
3	"	0·153	1·5	3.40	4.15	−3·9	46·8
4	"	0·156	2·0	3.43½	4.18½	−3·8	47·9

TABLE XVI.—*Influence of Sulphuric Acid on Rapidity of Inversion at 60°.*

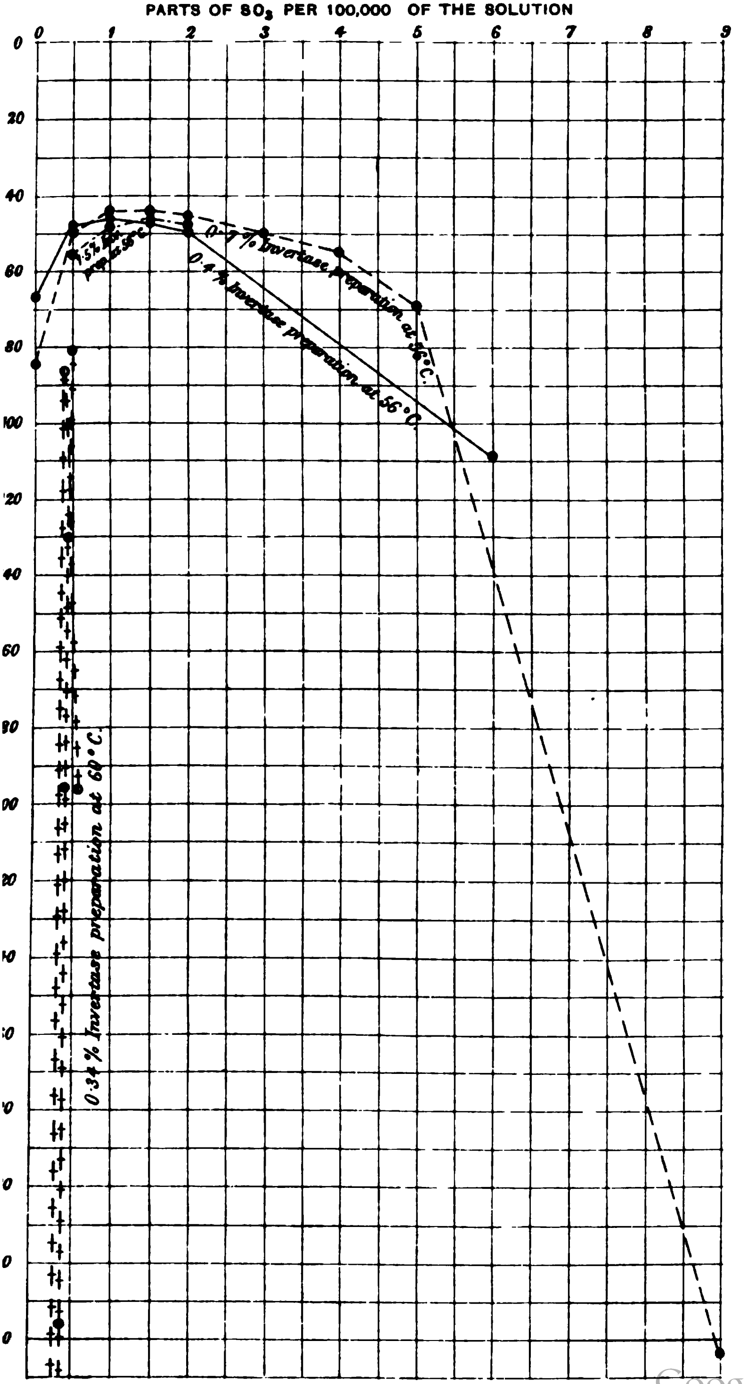
Sugar, 10 grams. Invertase solution, about 0·034 gram = 0·34 per cent. on sugar. Total solution, 50 c.c. Temperature, 60°. In Plate IV the curve is indicated by lines of crosses.

Experiment.	Series.	Invertase solution in grams.	SO_3, parts per 100,000.	Time of start.	Time of stopping.	Reading in 200 mm. tube.	Minutes to point of no optical activity calculated from 0·1 gram invertase preparation.
1	S	0·0343	0·2	3.29	6.18	+68·0	920·0
2	"	0·0343	0·4	"	"	+14·3	85·4
3	"	0·0343	0·6	"	"	+42·8	196·0
4	T	0·0342	0·3	11.38	3.22	+55·0	442·0
5	"	0·0342	0·35	"	"	+50·0	336·0
6	"	0·0342	0·4	"	"	+34·4	195·0
7	"	0·0342	0·45	"	"	+20·6	131·0
8	"	0·0342	0·5	"	"	+ 1·8	80·4

In Plate IV we have mapped out the results given in Tables XIII to XVI.

A study of Plates III and IV enables us to see the remarkable influence exerted by minute quantities of acid on the rapidity of the action of invertase: and it shows the absolute necessity, if we wish to obtain the greatest possible amount of work from a preparation of in-

V. THE INFLUENCE OF SULPHURIC ACID ON RAPIDITY OF INVERSION AT 56° AND 60° C.



vertase, of obtaining that degree of acidity which is most favourable for the action. The amounts of acidity involved are so extremely minute that it is absolutely necessary to ascertain this factor for each separate experiment. We have already referred to these facts under the heading "The Influence of the Proportion of Invertase Preparation Present."

From these Plates it will also be seen that the most favourable degree of acidity varies with the temperature and with the percentage of the active agent present. We may add that it is a different quantity for each different invertase preparation. We have not been able to find the law which governs these variations. In Table XVII we give approximately the most favourable amount of sulphuric anhydride for the invertase solution that we used. The numbers are inferred from the results recorded in Plates III and IV.

TABLE XVII.—*Comparison of the most Favourable Amounts of Sulphuric Acid.*

Invertase solution per cent. on the sugar.	Most favourable amount of SO_3 expressed in parts per 100,000 of solution.	
	Temperature 15·5°.	Temperature 56°.
0·4	—	1·25
0·7	—	1·25
1·5	7·5	1·5
4·5	15·0	—
15·0	25·0	—

These numbers do not seem to bear any relationship to one another, but it is evident that the more invertase is used the greater the amount of acid necessary; though the two are not in simple proportion. It is also noticeable that the higher the temperature, the less acid is required. We cannot see the reason of these variations. It is evident that they are not due to the inverting action of sulphuric acid *per se*, as these minute amounts are perfectly inactive at the temperatures employed. It is also remarkable how fatal to the reaction is a small variation in the acidity. In Table XVI it is shown that at 60° 2 parts per million of acid alters the rapidity of the reaction elevenfold.

The effect of alcohol is adverse to the reaction.—In Table XVIII the results of experiments are given in which we substituted alcohol for a portion of the water. These experiments were conducted in the manner already described.

Each beaker was made to contain 10 grams of sugar, 0·24 gram of invertase solution, and 0·4 c.c. of decinormal sulphuric acid. After the addition of the alcohol it was made up with water to 50 c.c. Temperature, 15·5°. Time, 9.39 to 12.18 = 159 min.

TABLE XVIII.—*The Influence of Alcohol on the Rapidity of Inversion.*

Beaker.	Alcohol, per cent. on the solution.	Reading in 100 mm. tube.	Per cent. inverted.	Minutes to point of no optical activity calculated for 0·1 gram invertase preparation.
1	0	0	74·1	382
2	0·25	+ 0·6	73·0	390
3	0·50	+ 2·0	70·3	412
4	1·00	+ 4·2	66·0	471
5	4·00	+12·0	51·0	713

We have now the means of comparing the influence of two foreign substances with the law laid down by Harcourt, namely, "It varies directly with some function of each of the other conditions under which the change occurs." Taking the alcohol first, it is evident from the following comparison that its influence varies in arithmetical progression with the amount present:—

Theory	382,	402,	422,	462,	702.
Found	382,	390,	412,	471,	713.

The agreement here is within the limit of the errors of experiment. We may note that the addition of 5 per cent. of alcohol about halves the rapidity of the reaction.

The case of sulphuric acid is different. It is at once evident that the influence of varying amounts of this substance is not at all in accord with the above-stated law of Harcourt. This fact is similar to that we mentioned under the heading "Influence of Temperature," namely, that Harcourt's experiments are not truly comparable with these, because they were not done with a substance which has a stimulating effect up to a certain percentage only, but afterwards has the opposite tendency. Possibly under these circumstances, too, the results obtained would accord with those here noted. It may be objected to this that the law, if it is accurate, precludes the possibility of such a reaction. This is true: but we must remember that the theory was based upon a few reactions only, and it by no means follows that some others may not have a point of maximum influence, and would therefore follow lines similar to this one. This is the more probable, because we can see from Plates III and IV that if we only examined the reaction some distance on either side of the maximum point, we should obtain numbers very similar to those which would be yielded by a reaction following Harcourt's theory.

Molecular Weight of Cane-Sugar undergoing Inversion.

Under the last heading we showed that if an alkali is added to a solution of cane-sugar undergoing inversion, the optical activity suddenly falls many degrees. It became, therefore, a question whether, in calculating the percentage of inversion, it was right to take as a basis the optical activity before or after this sudden change. With this object we determined the freezing point of a solution of sucrose that was undergoing inversion (Raoult's method, see heading "Molecular Weight of ζ-Invertan"), and compared it with the optical activity of the solution both before and after stopping with alkali. Theoretically the optical activity should have been determined and the sample should have been killed at the same moment that the solution was frozen. The two last factors were practically possible, but for the first the solution had to be warmed up before it could be observed. We did this as quickly as possible; the inversion proceeding during the interval can only have been slight, and the error introduced thereby would be such as to make the residual decrease appear smaller than it really was. It will be seen later on that this point is not material to the results. The experiment was conducted as follows:—

50 grams of cane-sugar, 3 c.c. of a solution of invertase, and 0·8 c.c. of decinormal sulphuric acid were dissolved together to 250 c.c. of solution at 11.51 A.M. The freezing point of the mixture was at once determined. As soon as this was done, the half frozen mass was rapidly thawed, and 20 c.c. of it was killed by pouring into a beaker containing a drop of the strongest potassium hydroxide. The unkilled portion was rapidly warmed and its optical activity taken as quickly as possible in the 200 mm. tube. After a short time, the optical activity of the portion killed by alkali was observed.

After this first series of observations had been made, all the portions which had not been killed were added together and allowed to stand in the cold for half an hour: a second similar series of observations was then made. In all there were five such series, the last of which was made the following morning, so that the solution had the whole night to complete the inversion. The following table gives the numbers obtained:—

TABLE XIX.—*Comparison of the Freezing Point and Optical Activity of Sucrose Solution undergoing Inversion.*

Series.	Time of freezing.	Freezing point.		Optical activity of the solution, divisions in 200 mm.		Residual decrease of optical activity calculated in per cent. of sugar.
		Observed.	Corrected.	Unkilled.	Killed.	
1	11.53	−1·49	−1·57	+74·5	+69·4	4·9
2	12.30	−1·86	−1·95	+57·9	+37·6	19 6
3	2.25	−2·58	−2·65	+ 0·6	−20·4	20·3
4	4.15	−2·74	−2·82	−19·1	−24·8	5·5
5	22 hours	−2·76	−2·84	−27·8	−27·8	none

The column "Freezing point, Corrected," gives the freezing point after allowing for the inaccuracies of the thermometer. The last column gives the amount of cane-sugar which apparently became inverted on adding the alkali (see "Influence of Foreign Substances"). It is calculated in percentages on the total sugar present.

During the process of inversion, the molecular weight of the sugar decreases from 342 to 180. The decrease in the intermediate stages is of course in proportion to the amount inverted, and therefore should be in arithmetical progression with the decrease of optical activity. The calculation of the molecular weight from the optical activity is therefore a simple matter. To take the first number, + 74·5 div., the original optical activity must have been 76·8 div.; so the decrease was 2·3 div. The total decrease when inversion is complete is 103·6 div., whilst the total decrease in molecular weight is 162.

$$103·6 : 162 :: 2·3 : 3·6.$$

3·6 represents the decrease in molecular weight corresponding to 2·3 div. decrease in optical activity. The molecular weight of the sugars would therefore be 338·4 (342 − 3·6).

In calculating the molecular weight from the freezing point, we must first make allowance for the effect of the alcoholic solution of invertase, &c., on the freezing point. The only practicable way of doing this is by taking the number obtained after standing 22 hours and (as we know that all the sugar is inverted) deducting the theoretical amount due to the invert-sugar present. The remainder we look upon as a constant error running through all the observations. The freezing point of a solution of cane-sugar containing 20 grams of sugar per 100 c.c. should be −1·27°. This figure would be increased to −2·71° after inversion, making allowance both for hydration and contraction. If we compare the latter number with the one obtained, 2·84°, we find a difference of 0·13, and this we look upon as the constant error. The conversion of these results into molecular weights by the ordinary means is difficult, because of the necessity of making allowance for the varying concentration of the solution due to hydration and contraction, but if we adopt the same method of calculation that we gave for the optical activity, the affair is simple. We take the theoretical number for the cane-sugar, −1·27°, and the numbers obtained between this and −2·71° are in inverse arithmetical progression with the molecular weights between 342 and 180. The calculation is the same as in the case of the optical activity. It will be noticed that the numbers obtained from the freezing point and from the optical activity are calculated quite independently of each other

Table XX shows the results of these calculations.

TABLE XX.—*Molecular Weight of a Sucrose Solution undergoing Inversion.*

Series.	Freezing point, deducting constant error.	Molecular weight of sugar calculated from the		
		Freezing point.	Optical activity before killing.	Optical activity after killing.
1	−1·44	323	338	330
2	−1·82	280	312	281
3	−2·52	201	223	190
4	−2·69	182	195	183
5	−2·71	180*	180	180

The first column gives the freezing point after allowing for the constant error.

It will be seen that the molecular weights obtained by Raoult's method agree extremely closely with those calculated from the optical activity after stopping the reaction with alkali, whereas they are throughout too low for the numbers obtained without stopping.

We can, therefore, only assume that the molecular weight is the same before adding the alkali as after, although the optical activity would indicate a considerable decrease in it, and we may further say that the optical activity of a solution undergoing inversion does not give a true measure of the amount of cane-sugar that has been split up into dextrose and levulose; but if the solution is stopped by an alkali, and time is allowed for the optical activity to become constant, it is a correct indicator of the amount of cane-sugar that has undergone inversion at the moment of stopping.

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* This number was assumed in the calculations, and is therefore of no value in the comparison.

Extent of the Power of Invertase.

The strongest sample of invertase we ever prepared reduced the optical activity of 100 times its own weight of sucrose to the zero point in 25·1 minutes; that is to say, it inverted 74 times its own weight of cane-sugar in 25·1 minutes. If a temperature of 54° had been employed, it would have inverted 7·5 times as much, = 550 times its own weight in 25·1 minutes, or at the rate of about 22 times its own weight every minute; and, provided that the invert-sugar could be occasionally extracted and replaced by cane-sugar, we have every reason to think that the invertase would go on inverting at this rate for an infinite time. Many samples have been obtained nearly as strong as this.

To test whether there is any limit to the action of invertase, we made a considerable bulk of cane-sugar solution, and added to it the requisite minute amount of sulphuric acid. It was then boiled in a large flask, a small sample of it was taken in a small flask, and the two flasks were then placed side by side in a water-bath at 50—54°. A very small weighed quantity of invertase solution was added to the larger flask, and the two were kept at the above temperature for a fortnight. At the end of this time the blank experiment showed about 10 per cent. of the sugar inverted, while we found, after making allowance in the large bulk for this amount, that the invertase had acted upon over 100,000 times its own weight of the sucrose. Inversion was still proceeding slowly.

Comparison of the Laws governing Inversion with Harcourt's Laws.

Having now given in sufficient detail the results of our experiments on the action of invertase on sucrose under various conditions, and having shown in each case to what extent they agree with those laws which Harcourt found to regulate the chemical action of inorganic substances, we now proceed to review the comparisons as a whole.

We will, in the first place, sum up the results.

I. *The Rapidity of the Reaction.*—This agrees very closely with Harcourt's law, but we find that there is some slightly disturbing cause at work which varies in strength during the course of the reaction, and which we have not been able to discover.

II. *The influence of the proportion of invertase preparation present* agrees exactly with the theory.

III. *The influence of the concentration of the solution* does not agree with Harcourt's results; but we have pointed out that the experiments are not comparable.

IV. *The Influence of Temperature.*—At low temperatures, the reaction follows the theory very closely, but at temperatures approaching those at which the activity is destroyed the agreement ceases. We have put forward considerations to show that this result is such as might be expected.

V. *The Influence of Foreign Substances.*—The influence of varying proportions of alcohol is in exact accordance with Harcourt's law, but sulphuric acid gives results which by no means tally with it. In this case also we have accounted for the discrepancy by showing that the experiments are not comparable.

We can sum up these results by saying that Nos. I, II, and parts of IV and V agree with Harcourt's laws; but No. III and the remainder of IV and V do not agree, and that this disagreement may be accounted for by the fact that the conditions of experiment are not comparable.

From this we do not hesitate to draw the conclusion that the action of invertase on cane-sugar is governed by laws similar to those which govern simple inorganic reactions, and therefore we may safely conclude that it is a simple chemical action differing in no important way from the reactions of inorganic substances, and that there is no reason whatever for supposing that vital force enters in any way into the action.

Method of Estimating and Recording the Activity of Preparations of Invertase.

Before any attempt could be made to isolate invertase, it was, obviously, of the greatest importance to establish a trustworthy and practical standard method of measuring the inverting power of any given material. Indeed, as the inverting power is the only known attribute by which invertase can be recognised, so it is the only means we have of judging the amount of the substance present. A study of the laws which govern the reaction shows that the time factor is the most convenient one for expressing the intensity of this function, because the time that is necessary for a sucrose solution to reach a given percentage of inversion is in inverse proportion to the amount of invertase present. In the preceding work we have always, where possible, employed a solution containing 20 grams of sucrose per 100 c.c., and we have expressed the results in minutes necessary to reach the point of no optical activity. We have generally, also, calculated the results so as to allow for the different proportions of invertase preparation employed, taking the standard amount of the preparation as 1 gram per 100 grams of sugar. It now only remains to fix the standard temperature; we take 15·5° as being the most convenient. It is needless to remark that the experiment is always supposed to be conducted under the most favourable possible conditions of acidity; otherwise the results are of no value.

For results thus obtained we use the expression $\pm 0 = x$ min., x being the number of minutes that the invertase preparation takes to do a certain standard amount of work. The amount of invertase present in a given sample is, of course, in inverse proportion to the value of x, and hence, if this factor is known, it is easy to calculate the relative amounts of invertase contained in two or more inverting preparations.

We repeat that, in the formula $\pm 0 = x$ min., ± 0 is a certain standard amount of work, and x is the time that is taken to do it.

The standard conditions of the work are as follow:—

1 gram of the invertase preparation and 100 grams of sucrose, together with the amount of sulphuric acid most favourable for inversion, are dissolved to 500 c.c. of solution, and maintained at a temperature of 15·5°. The standard amount of work is the inversion of 74·1 grams of sucrose under these conditions. This is equivalent to reducing the optical activity of the solution to ± 0.

The practical method of ascertaining the value of x is very simple. 50 grams of sucrose is dissolved in water to nearly 250 c.c. solution, and put into a water-bath carefully maintained at 15·5°. When the temperature is constant, 0·5 gram of the material to be examined is added, and the time noted. The solution is then quickly made up to 250 c.c. and poured into five beakers placed in the water-bath. The five portions need not be accurately equal. To these beakers the following amounts of decinormal sulphuric acid (1 c.c. = 0·008 gram SO_3) are added, 0·1, 0·3, 0·6, 1·0, and 1·4 c.c. These numbers may be varied in any way that is thought best for the particular sample that is under examination. After standing an hour at 15·5°, the reaction is stopped in a small quantity taken from Beaker 3 by adding a few drops of strong potassium hydroxide, and the time of doing so is noted. A reading of this is taken in the polarimeter, and from this the percentage of sugar inverted is calculated by the formula already given ("Mode of Procedure"). The time which the contents of Beaker 3 will take to reach optical inactivity is calculated in the same manner as was given in the calculation of Table V (A column). It would be more accurate to use Esson's equation for this purpose: but it takes considerably longer than our way of calculating, and the results are practically identical. When the calculated time approximately arrives,

w drops of potassium hydroxide solution are added to each beaker,
the time accurately noted. The beakers are then allowed to stand
arter of an hour in order to allow the residual decrease to take
e, and a reading of each is then taken in the polarimeter. If the
bers thus obtained are such that some amount of sulphuric acid
ide the above series would give still more advanced numbers,
h will be obvious on inspecting the results, the experiment must
peated with more suitable quantities of sulphuric acid.

the five readings obtained for the above experiments, only the
hich shows the greatest amount of inversion is calculated. This
ne in exactly the same manner as described in arriving at the
ers in the A column of Table V, and the result gives the number
nutes equivalent to x.

circumstances are sometimes such that it is necessary to per-
the experiments under conditions different from the standard
The variation may be either in the amount of invertase used, or
emperature at which the inversion takes place. It is convenient
the percentage of inverting material when it is either a very
or a very weak preparation. It is generally best so to arrange
unt of material that the point of no optical activity is attained
one to three hours. If any proportion of invertase different
standard amount is employed, it will be necessary to correct
ber calculated as above in accordance with the rule that the
in inverse proportion to the amount of invertase preparation
l. In Table V, the figures corrected for this factor are given
n B. In the case of a determination of the inverting power
t is not possible to get even approximate results in the cold;
ndard temperature has to be discarded in favour of 54°. At
erature, yeast gives trustworthy and constant results, per-
parable among themselves, though whether the whole of
ase contained in the yeast is brought into action is doubtful,
all show under the heading "Liquefaction of Yeast."
rticulars of the action of yeast at this temperature will
a future paper.

nation of the inverting power of yeast or any other mate-
ich a high temperature is desirable, is otherwise conducted
he same way as we have described above. The cold yeast
ectly into the sugar solution at a temperature of 54°, and
is kept at this temperature during the whole reaction—
re or less is not of paramount importance. Very much
nts of sulphuric acid are required: about 0·0, 0·05, 0·1,
of decinormal sulphuric acid are the best amounts for
kers. After calculating the results obtained by this
necessary to correct them for the temperature. This is

done by multiplying the number of minutes by 7·5, which brings the results to the standard condition.

In ordinary approximate estimations of the strength of a sample of invertase, we have only, as a rule, used three beakers, instead of five. The method remains, of course, the same, but proportionate amounts of sugar, invertase, &c., must be taken. For the amounts of decinormal sulphuric acid we generally take 0·0, 0·4, and 0·8 c.c.

It should be noted that if the invertase preparation to be tested is in solution, it is advisable to have it as free as possible from alcohol, because this has, as we have shown, a deterrent action on the progress of the reaction. However, as the solution cannot contain more than about 20 per cent. absolute alcohol, the effect produced by it will scarcely be perceptible, if not more than 0·5 c.c. is employed to each beaker. We have generally partially freed from alcohol by allowing the solution to stand all night in a vacuum over sulphuric acid.

Many instances of the way in which this method of estimation is used in practice will be found later on.

In order to show the reliability of the method, we cannot do better than give some results obtained with a solution of invertase which was kept for a long time in a stoppered bottle. From the dates given it will be noticed that the experiments were made at irregular intervals during nearly two years. The reason for this is that they were not made with the object of testing the accuracy of the process, or, indeed, even with that of estimating the inverting power of the solution: but they are results which were obtained incidentally in the course of our investigations, and the majority of the figures have been given in the previous tables.

TABLE XXI.—*Estimations of the Inverting Power of a given Solution of Invertase Preparation under widely varying conditions.*

No.	Date.	Temperature.	Invertase solution per cent. on sugar.	SO_3, parts per 100,000.	Minutes.	Optical activity in 100 mm. tube	± 0 = min.
1	May, 1888..	54·0°	0·42	1·0	163·5	−6·2	344
2	”	54·0	0·7	1·0	67·5	−1·3	330
3	”	54·0	1·53	1·5	35·0	−1·95	351
4	Feb., 1889..	15·5	1·5	7·5	272·0	−0·7	390
5	”	15·5	4·5	10·0	154·0	−7·8	415
6	April, 1889.	15·5	15·0	30·0	25·0	+3·75	357
7	”	54·0	0·345	1·0	103·0	+8·25	414
8	May, 1889..	15·5	2·0	2·0	182·0	−0·2	358
9	”	54·0	0·25	trace	204·0	−0·1	383
10	Aug., 1889..	15·5	2·4	2·0	159·0	0	382
11	Jan., 1890	15·5	1·8	4·0	198·0	+5·0	398

The first thing that strikes us on examining this table is the remarkable agreement of the numbers for x in the column $\pm 0 =$ min.; they differ, no doubt, somewhat, but when we consider the various conditions under which they were arrived at, we must admit that the agreement is remarkable. First, they were obtained for the same preparation of invertase at intervals during two years; secondly, the experiments of which they express the results were made at different temperatures; and, thirdly, the amount of preparation employed varied from 0·25 to 15·0 per cent. on the sucrose. When we add to these considerations the fact that the time taken by the experiments varied from 25 minutes to 272, and that a slight error in taking the time materially affects the results for the shorter times, while it has little effect on those for the longer ones, it will be conceded that the numbers are sufficiently concordant to establish the method of determination and record.

It will be noticed that between Nos. 3 and 4 there is an interval of nine months, and this corresponds with a considerable increase in the minutes necessary to reach ± 0. This probably indicates an actual decrease in the inverting power of the solution, as a slight precipitation took place during this period.

It is with the above solution that practically all our investigations on the hydrolytic power of invertase were conducted. We called it the "A" sample of invertase, and the method of its preparation is given under the heading "Separation of Invertase from Yeast Liquor."

In concluding this description of our method of estimating the activity of a material containing invertase, we should like once more to state that when we use the expression $\pm 0 = x$ minutes, we mean that the given inverting material takes x number of minutes to do a certain standard amount of inversion under certain standard conditions. What these standards are, and why we chose them, we have already described. We may further state that the number, x, obtained by our method is a perfectly reliable number, and that it varies in inverse proportion to the amount of invertase contained in the material or materials under examination.

PART III.—THE PREPARATION OF INVERTASE.

Liquefaction of Yeast.

Having clearly shown the method by which a quantitative expression can be given to the function of invertase, and thus established a factor for describing the relative quantity of the substance in different materials or preparations, we now proceed to describe our efforts to prepare it in a pure state. A sample of brewers' ordinary pressed top fermentation yeast was obtained from Messrs. Bass & Co. The inverting activity was estimated by the method before described, and it was found to be ± 0 = 2020 minutes. The yeast was then allowed to stand at a temperature between 15° and 20° for seven days. At the end of this time it had become a thick, yellow liquid; the smell arising from it was not disagreeable, and it was evident that the change occurring was not ordinary putrefaction. It was thrown upon a filter, when a clear, yellow liquid filtered through. The strength of this was found to be ± 0 = 7100′, so that it only possessed about 30 per cent. of the power of the original yeast. The soft, yeasty mass remaining on the filter was pressed between blotting-paper, and then its strength was found to be ± 0 = 1020′, or twice that of the original yeast. This shows that although the yeast had given up most of the water it contained, yet the greater part of the active agent was still confined to the cells.

The partially dry residue was left for another 10 days at the same temperature as before, and was then made up with water to the same bulk as the original yeast occupied after it became liquid. It was well mixed and then filtered. This time the inverting power of the filtrate was ± 0 = 1470′, which shows that the yeast cells now allowed the invertase to pass freely out of them; indeed, there is an apparent increase in the amount of invertase present, even after allowing for the separation of the insoluble portions of the yeast; this is always the case, as will be shown further on.

Another sample of yeast was obtained, this time from a stout brewing, also by Bass & Co. The activity was estimated by the method before described, as follows:—50 grams of cane-sugar was dissolved to nearly 250 c.c. of solution, and the temperature adjusted in the constant bath to 54°. At 9.35 A.M., 0·5 gram of the pressed yeast was added and thoroughly mixed. It was now without delay fairly equally divided among five beakers of equal size, placed in the bath, and varying amounts of sulphuric acid added.* At 11.31 A.M., 116 min. from the start, the reaction was stopped by adding a few drops of potash solution to each beaker, care being taken that each one was alkaline. The beakers were then placed on one side to cool. When cold, each one was made up to 50 c.c., a little of the solution passed through a filter, and the optical activity taken.

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* In cases where the inverting power of the preparation is approximately known, it is not always necessary to make the preliminary trial of Beaker 3, which we described under the previous heading. We omitted it in this and most of the following estimations.

Beaker.	C.c. decinormal H_2SO_4.	Reading in 100 mm. optical activity tube.
1	nil	+ 3·9
2	0·1	+ 5·4
3	0·15	+ 8·0
4	0·2	+ 9·6
5	0·3	+12·2

From this it will be seen that Beaker 1 was in approximately the most favourable condition as regards acidity. The difference between 2 and 5 is 6·8 div., or 3·4 div. per 0·1 c.c. decinormal sulphuric acid, whilst between 1 and 2 it is only 1·5 for the same amount of acid. A glance at Plate IV (page 858) will show that the curve is a very sharp one, and there is no doubt that Beaker 1 was about at the top, and it was only necessary to calculate the results obtained from it. The reading + 3·9 represents 66·6 per cent. inverted, $(38{\cdot}4 - 3{\cdot}9) \div 0{\cdot}518 = 66{\cdot}6$.

66·6 per cent. inverted, referred to the time curve (see Plate I), gives 10·4 T (T = time units). On the same curve $\pm 0 = 12{\cdot}7$ T. Now the 10·4 T took 116′; how many will 12·7 T require?

$$10{\cdot}4 : 12{\cdot}7 :: 116 : 141{\cdot}7.$$

We must still multiply by 7·5 to compensate for the temperature. $141{\cdot}7 \times 7{\cdot}5 = 1063$. The freshly pressed yeast had, therefore, an activity $\pm 0 = 1063'$.

The yeast was placed in a covered beaker and allowed to stand for a month at a temperature of 15—20°. At the end of this time it was quite liquid, but the smell was not at all disagreeable. Its activity was determined again in the same manner as before, but, as we had the former experiment to guide us, only two beakers instead of five were used. The time was 131′, and the results were as follows:—

Beaker.	C.c. decinormal H_2SO_4.	Reading in 100 mm. tube.
1	nil	−3·4 div.
2	0·1	−3·5 „

The acidity was evidently at the most favourable point. The observation made for Beaker 2 was calculated as before.

$$-3{\cdot}5 \text{ div.} = 80{\cdot}9 \text{ per cent. inverted} = 15{\cdot}7 \text{ T.}$$

Then $$15{\cdot}7 : 12{\cdot}7 :: 131' : 106'.$$

$$106 \times 7{\cdot}5 = 795'.$$

So that the pressed yeast which when fresh had an activity $\pm 0 = 1063'$ had increased its power on standing a month to $\pm 0 = 795'$.

It will be noticed that in this case also there is an apparent increase in the invertase of yeast on standing. Evidently this increase must either really take place, or else our method of estimating the invertase of *fresh yeast* does not give sufficiently high results. We do not deny that the former explanation is very probable, but we are inclined to attach more importance to the latter, because we have noticed that when the yeast in the liquefied mass is quite dead, and, therefore, presumably incapable of forming invertase, a further apparent increase of this substance is caused by filtering. We give an example of this later on. Whichever be the true explanation of the increase, we can say with confidence that the results obtained by our method of estimating the inverting activity of yeast are constant numbers, and perfectly comparable among themselves.

It is evident from the above that sound pressed yeast does not putrefy on keeping, as has generally been supposed. Pressed yeast from winter brewings kept for a month at a temperature of 22° becomes very liquid, but is free from bacteria except on the surface, where there is a comparatively small growth of bacilli, which causes it to darken. Underneath this the yeast retains its original colour and smell. We have known summer-grown yeast under the same conditions to develop large quantities of *acetic acid* while liquefying, but apparently there was no other change. A microscopical examination at this stage shows that the yeast cells have shrivelled up into a comparatively small bulk, whilst their outline is irregular and ill-defined. The cell wall has almost entirely disappeared, but the large majority of the cells are unbroken. The vacuole occupies practically the whole of the interior of the cell, and the granulations are very marked, being, in fact, by far the most distinct feature of it. There are at times a few—a very few—bacteria present, resembling *Bacillus subtilis*. In great contrast to the shrivelled yeast cells, there are a few cells that seem to have changed very little; their walls are dark and thick, and they themselves are round. Nearly the whole of the interior of these cells is occupied by the vacuole, but there are absolutely no granulations. These cells—comparatively few in number—stand out very distinctly from the rest, and as no intermediate stages are to be seen, it seems probable that they are a distinct species.

Kept for a longer time, say a couple of months, a growth of blue mould slowly appears on the surface of the liquid yeast; but this does not seem to impair the activity of the invertase. The yeast liquor, as we call the fluid obtained from the liquefied yeast, soon assumes a somewhat darker tint, but shows no other sign of decomposition. This immunity from putrefaction is probably partly due to the concentration of the solution, as dilution with water causes it to become black and putrid. We have seen a sample of yeast that was washed at the end of the first seven days, and then pressed, become black and smell badly, in a short time, whilst almost the whole of the inverting power disappeared. The sp. gr. of the liquid mixed with the dead yeast cells is about 1080; this concentration alone would not be sufficient to prevent putrefaction; there must, therefore, be some antiseptic present. No doubt the hop resins present—the yeast is always exceedingly bitter—act as a preservative. If at the end of seven days from the start, 30 per cent. of absolute alcohol is added, no further change takes place; the yeast cells do not give up their invertase, and filtrates obtained later are only slightly active.

The following experiment shows quantitatively the distribution of the invertase during the liquefaction and filtration of yeast:—

Some yeast from an ale of or. gr. 1068 was pressed and allowed to liquefy for a month. At the end of that time its activity was estimated, with the following results:—

Beaker.	C.c. decinormal H_2SO_4.	Readings in 100 mm. tube.
1	nil	+11·3 div.
2	0·1	+ 9·7 „
3	0·2	+10·5 „

Time, 3.38 to 5.40 = 122 min. Temperature, 54°. Calculation for No. 2 beaker, + 9·7 divisions = 55·4 per cent. inverted = 7·7 time intervals.

$$7{\cdot}7 : 12{\cdot}7 :: 122 : 201.$$
$$201 \times 7{\cdot}5 = 1508.$$
$$\pm 0 = 1508'.$$

The water in the liquefied mass was also estimated. Weight taken, 1·466 grams. After drying it was 0·400 gram = 27·2 per cent. of solids and 72·8 per cent. of water.

The liquid was filtered. The filtrate or yeast liquor was slightly alkaline, and gave the following results:—

Beaker.	C.c. decinormal H_2SO_4.	Readings in 100 mm. tube.
1	0·05	+4·8
2	0·15	+5·0

Time, 3.24 to 5.31 = 127′. Temperature, 54°.
Calculation for No. 1 beaker.

$$+4{\cdot}8 \text{ divisions} = 64{\cdot}9 \text{ per cent. inverted} = 9{\cdot}9 \text{ T}.$$
$$9{\cdot}9 : 12{\cdot}7 :: 127 : 163.$$
$$163 \times 7{\cdot}5 = 1223.$$

The activity of the yeast liquor was therefore ± 0 = 1223′.

We estimated the total solids. Solution taken, 4·17 grams. Solids dried at 100° = 0·933 gram. Ash = 0·109.

This is equal to 22·4 per cent. total solids containing 2·6 per cent. of ash and 19·8 per cent. of organic matter.

We have then the following comparison:—

	Liquefied yeast.	Yeast liquor.
Inverting power..........	1508′	1223′
Water..................	72·8 per cent.	77·6 per cent.
Solids..................	27·2 „	22·4 „

Now if 77·6 grams of water hold 22·4 grams solids in solution, 72·8 would hold 21·0 grams.

77·6 : 72·8 : : 22·4 : 21·0.

This leaves 6·2 grams solids (27·2 − 21·0) in an undissolved state in the liquefied yeast = 22·8 per cent. on the total solid matter. From this we can calculate what we should expect the inverting activity of the yeast liquor to be by simply allowing for the 6·2 per cent. of undissolved solids in the liquefied yeast.

100 : 93·8 :: 1508 : 1414.

Calculated activity of yeast liquor	± 0 = 1414′
Actual „ „	± 0 = 1223′

So that there was a considerable increase in activity on filtration, as has been already pointed out.

We now have the following figures for the yeast:—

Water......................	72·8 per cent.
Dissolved solids	21·0 „
Undissolved solids..........	6·2 „
	100·0 „

Inverting power of the liquefied yeast........	± 0 = 1508′
„ „ calculated for the yeast liquor	± 0 = 1414′
„ „ found „ „	± 0 = 1223′

The solution thus derived from yeast has a somewhat high colour, which increases slightly on standing. Its odour is not unpleasant, by no means reminding one of putrefaction. If prepared from yeasts obtained from winter brewings, it is always slightly alkaline, but in summer it sometimes contains a considerable amount of acetic acid. It will keep for a long time unchanged and without any marked diminution of its inverting power, but in time, if left exposed, blue mould grows on it, especially in summer.* It throws down a precipi-

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* Since writing the above we have examined a sample of yeast liquor prepared nearly a year ago, and kept since then in a stoppered bottle. There is a small growth of mould on the surface, otherwise it is still perfectly sound and active.

ɔoiling. It is partly precipitable by alcohol, and it yields
ılent copper compound described further on. We have taken
fic gravities of three different samples of yeast liquor as fol-
\, 1082; B, 1076; C, 1080; but they naturally contain a
ɔhol.

Separation of Invertase from Yeast Liquor.

ıg thus far demonstrated that the whole of the inverting
an be obtained in the yeast liquor by the method described,
t step was to determine whether the solid matter in solution
liquid could be fractionated without loss of inverting power.
eptember, 1887, some pressed yeast was kept for 11 days at
erature of 13° to 15°. It was then well mixed up. After
.g for a few hours, a little clear liquid again showed itself
surface. A portion of this was sucked up in a pipette, and its
ng power determined by the side of that of a sample of the
ixed mass of liquefied yeast. The results were—supernatant
± 0 = 4000′; the mixed liquid yeast ± 0 = 2020′. It was
tly not yet nearly ready for filtration.
ee days later—14 days from the start—the activity was again
ted as before. The supernatant liquid gave ± 0 = 2410′; the
liquefied yeast, 1660′. This also shows the increase in the
ing activity of the liquefied yeast already remarked upon.
.iquefying mass was now allowed to stand for two months
r; at the end of that time it was well stirred up and filtered.
invertive power of the filtrate was found to be ± 0 = 1200′,
showing a higher activity than the whole mixture had at the
f 14 days. We, therefore, considered that we had the invertase,
ıst in greater part, in solution.
the filtrate, sufficient alcohol was added to produce a precipi-
this was allowed to deposit. The alcoholic solution was de-
ɔd off the semi-liquid precipitate, and the activity of both was
ıated. Alcoholic solution, ± 0 = 14100′; thick semi-liquid pre-
ate, ± 0 = 370′.* The alcohol was evidently not quite strong
ıgh to precipitate the whole of the invertase, though the amount
aining in solution was very small, as was indicated by the invert-
activity. The precipitate was dissolved in the least possible quan-
of water, and the solution filtered and put by with a little
hol in a stoppered bottle. The solution contains 13·6 per cent. of
anic matter and 1·7 per cent. of ash.† It is with this solution

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Probably the real activity was greater than this. At the time this experiment
made, we were not aware that it was necessary to estimate the activity under
most favourable conditions of acidity.

We shall refer to this as the "A" sample of invertase.

that nearly all our experiments on the hydrolytic action of invertase have been done. Its strength at different periods is given in Table XXI (p. 868).

The following is a more detailed account of the preparation of invertase from yeast liquor. The whole experiment was quantitative, and the inverting power was carefully followed to show that none was lost during the purification.

The yeast liquor employed was the last described under the heading "The Liquefaction of Yeast;" its inverting power was there shown to be ± 0 = 1223′. It will be remembered that this estimation was not done at the standard temperature of 15·5°, but at 54°, and an allowance made for the difference. It was thought wise to do another estimation under standard conditions.

Beaker.	C.c. decinormal H_2SO_4.	Reading in 100 mm. tube.
1	0·4	+1·0
2	0·6	+0·5
3	0·9	+0·1

Time, 3.30 to 5.31 = 121′. Temperature, 15·5° (standard). Sucrose, 30 grams in 150 c.c. solution. Amount of invertase solution used, 3 grams = 10 times the standard quantity. No. 3 beaker was evidently at about the most favourable acidity, and as the reading was practically ± 0, it only remains to multiply the minutes by 10 to allow for the amount of the invertase solution used, and we get ± 0 = 1210′. Comparing this with the number we got at 54°, ± 0 = 1223′, we find an agreement so close that it shows in a striking manner the accuracy of the method of estimation.

The sp. gr. of the solution was 1080. The total solids, we have already seen, amounted to 22·4 per cent., of which 2·6 per cent. was ash, and 19·8 per cent. organic matter. On 100 c.c., weighing 108 grams, this would amount to 24·2 (22·4 × 1·08) grams total solids, consisting of 2·8 grams ash and 21·4 grams organic solids. This is more than might be expected from the gravity, but there is, no doubt, a considerable amount of alcohol in the solution. Its inverting power was ± 0 = 1210′, which, reckoned on the organic solids, is equal to ± 0 = 240′ (100 : 19·8 : : 1210 : 240).

100 c.c. of this yeast liquor was now precipitated very slowly, and with frequent pauses, with alcohol of 70 per cent. (0·87). As soon as a precipitate appeared, the solution was allowed to stand for a couple of hours, and then some more alcohol of the same strength was added, and so on, until no further precipitate was produced. By this means the precipitate was obtained in a finely-divided state, and with a minimum of impurities. The solution was allowed to stand for two days, and then it was decanted and the precipitate washed several times

by decantation with 47 per cent. (0·925) alcohol. It was then thrown on to a filter, and again washed with the same alcohol and allowed to drain. The washed precipitate was carefully transferred to a beaker and made up with water to 100 c.c. It was by no means all soluble; a light, finely divided, and slightly coloured precipitate remained. It was well mixed with the solution, and the total solids estimated. 3·425 grams of solution gave 0·144 gram dried at 100°, of which 0·018 gram was ash. This gives for the whole of the turbid solution 3·68 grams organic solids and 0·53 gram ash. So the matter which had been discarded in the alcohol amounted to 17·72 grams organic solids (21·4 − 3·68) and 2·27 grams ash (2·8 − 0·53).

The turbid liquid was now filtered, and the insoluble portion discarded without washing. It consisted of *yeast albuminoïd*, and is described under that heading.

The filtrate, after the separation of this insoluble albuminoïd, was clear and almost colourless; it readily yielded the characteristic copper compound which we shall describe fully later on.

Estimation of total solids and ash in the clear solution:—3·300 grams solution gave 0·071 gram total solids dried at 100° and 0·011 ash, leaving 0·060 gram of organic solids. This gives 1·82 cent. of organic solids and 0·33 per cent. of ash.

So that the insoluble albuminoïds which we had filtered out consisted of 1·86 grams (3·68 − 1·82) organic solids, and of 0·2 gram (0·53 − 0·33) ash.

The optical activity of the organic solids in solution was $[\alpha]_j = +74°$. The inverting power was estimated under standard conditions, but with 10 times the standard weight of the solution.

Beaker.	C.c. decinormal H_2SO_4.	Reading in 100 mm. tube.
1	0·6	−1·5
2	0·9	−0·8
3	1·2	+1·0

Time, 2·48 to 5·19 = 151′. The calculations for Beaker 1 are −1·5 = 77 per cent. inverted.

This is equal to 13·9 T. 13·9 : 12·7 :: 151 : 138.
138 × 10 = 1380.
± 0 = 1380′.

This, calculated on the organic solids in the solution, gives—

± 0 = 25·1′ (100 : 1·82 :: 1380 : 25·1).

We can now calculate how much of the inverting power has been lost during these processes. As the volume of the purified solution was the same as that of the yeast liquor used, the inverting activity of the two should agree if no inverting power was lost. The yeast liquor had an activity of ±0 = 1210′, the purified solution ±0 = 1380′, showing a loss of 12·3 per cent. of the total inverting power.

This is a most satisfactory result when we take into consideration the fact that precipitation by alcohol has a strong tendency to destroy invertase, as will presently be seen. We must also remember that nearly pure solutions of invertase will not long retain their activity, as will be shown later.

Under these circumstances the loss of 12·3 per cent. of the invertive power must be considered small and such as can be fairly attributed to the treatment; hence, we have satisfactorily proved that all the invertase originally present in the yeast is contained in the clear filtrate described.

In Table XXII the constitution of the 100 c.c. yeast liquor and of the yeast whence it was derived is given.

The ash, which is principally a mixture of potassium and magnesium phosphates, is all put together, as its presence in the various precipitates and solutions is probably purely accidental, and depends on the amount of washing, &c., they have been subjected to. This at least is the case with invertase, as will be shown later on.

TABLE XXII.—*Composition of Yeast and Yeast Liquor.*

The constituents of yeast.	Per cent. on the dry solid matter of the yeast.	Grams per 100 c.c. of the yeast liquor.	Inverting activity calculated on the yeast liquor.
Matter Undissolved in Yeast Liquor.			
Cellulose and other organic matter	22·80	—	—
Matter Dissolved in Yeast Liquor.			
Organic matter soluble in alcohol of 47 per cent.	56·53	17·72	none
Yeast albuminoïd	5·93	1·86	none
Organic matter insoluble in alcohol, soluble in water (invertase)	5·81	1·82	1380′
Ash	8·93	2·80	—
Total............................	100·00	24·2	1210′

In the first column of figures we give the amounts of the constituents of the yeast calculated on the total dry solid matter. In this case we have taken it for granted that all the water in the thoroughly liquefied yeast holds in solution an equal amount of the various solid constituents. That this is so we cannot be quite certain, as there may be a different solution in the interior of the dead cells. We, however, believe the mixture to be complete. It is difficult to see how the cell could allow a non-dialysable substance, like invertase, to escape so freely without the rest of the cell contents being equally diffused through the whole mass. The ash, too, which, calculated in this manner comes to 8·93 per cent., agrees very closely with the amount found in the original pressed yeast, viz., 8·75 per cent.

The 56·53 per cent. organic matter soluble in dilute alcohol and in water we neglected, having satisfied ourselves that it did not contain invertase.

This sample of invertase,* with an inverting activity of ±0=25·1′, is the purest we have ever been able to obtain. Many other preparations were made in the same way, but we have not again succeeded in obtaining one with an activity as high as this; the nearest approach to it being samples with an activity ±0 = 27·9′ and 28·5′. These numbers, however, agree moderately well with those obtained for the strongest sample. When we take this into consideration, and other facts to which we shall refer later on, we believe we are justified in concluding that the solid matter in the solution with the activity ±0 = 25·1′ was invertase contaminated simply with the products of its own decomposition from the 12·3 per cent. of lost activity, and with ash.

It will be seen that by the above method we have a ready means of obtaining large quantities of invertase. At one time we prepared 1 kilo. of dry invertase for the purpose of this work: but as we did not know its properties so well then as we do now, the preparation was not nearly so active as the above, though we have reason to believe that the only impurities were the ash and the products of the decomposition of the invertase. In the preparation of this we proceeded as follows:—

A small unheaded cask was filled about two-thirds full of pressed yeast and allowed to stand, covered with a towel, in a warm place for a month. The liquid mass was then passed, in small portions at a time, through a screw filter-press. This is a matter of time, as the solution only comes out with great slowness—even under considerable pressure. As the clear solution was obtained, alcohol was added to raise the whole to a 47 per cent. (0·925) solution of absolute alcohol, and the mixture allowed to stand for two days. At the end of that time the supernatant liquid was quite inactive. Stronger alcohol only brings down more ash. This liquid was decanted off and discarded, and the precipitate allowed to settle in tall vessels. To this dense precipitate a little water was slowly added until it became pasty, showing that the invertase was redissolved. This was diluted with some 28 per cent. alcohol (0·960), and the whole well mixed to ensure there being no lumps. Alcohol of this strength is necessary —among other reasons—to get the large insoluble precipitate of albuminoïd into such a state that it will not stop up the filter. The mass was then thrown on to a filter, allowed to drain, and washed with 28 per cent. alcohol. The filtrate was clear, and not much coloured; it was again made up to an alcoholic strength of 47 per cent.; the precipitate thus obtained was dehydrated with absolute alcohol, and dried in a vacuum over sulphuric acid, and powdered. The straw-coloured powder so obtained did not redissolve to a clear solution, and it contained 5·1 per cent. of ash. The analysis of the body free from ash was as follows:—N = 6·2 per cent., C = 46·5 per cent., H = 6·91 per cent. When first made it was very active, but in a few months its activity completely disappeared, and the powder was only partly soluble.

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* We shall refer to this as the "B" sample of invertase.

This large bulk was used in the preparation of most of the members of the invertan series.*

Since making the above preparation we have made many experiments with a view to obtain invertase in a greater state of purity. We have always found that every precipitation by alcohol means some loss of inverting power: and we shall presently show that when the invertase approaches a pure state, precipitation by alcohol destroys it entirely. We have, therefore, tried the effect of precipitating only once, and then thoroughly washing the precipitate with 0·920 alcohol. This we have found by far the most effective method. If alcohol weaker than 0·920 is used it generally destroys the invertase; and if the yeast liquor is precipitated very slowly in fractions, the result is often the same.

The mode of procedure we have found most effective in obtaining the highly active preparations of invertase is as follows:—Yeast is allowed to liquefy for at least a month in a fairly warm room. It is better not stirred, as the surface may become mouldy or putrid if the yeast has not been well pressed. At the end of this time the surface is removed, and any liquid on the top poured away; as far as our experience goes, the lower part will be found to be perfectly sound. This is thrown on to a quick filter, and after a couple of days the yeast liquor will have drained from it.

To the clear filtrate, alcohol, sp. gr. 0·870, to the extent of 1½ times its bulk is gradually added, with vigorous and continued stirring; in this way a precipitate is obtained which can be easily washed. After this mixing, which should take about half an hour, the solution is allowed to stand for 24 hours. The light precipitate will then have settled, and should be washed on this and several successive days by decantation with 0·920 alcohol. When the washings become nearly colourless, the precipitate is thrown on to a filter and allowed to drain, and immediately taken off, and again mixed with a large bulk of 0·920 alcohol. The precipitate is again collected; the filtrate should be colourless. The residue is mixed with its own bulk of water and some 0·970 alcohol. It is thoroughly incorporated, allowed to stand for a few hours, and then thrown on a filter. The filtrate contains the invertase.* The residue on the filter may be taken off and washed again with 0·970 alcohol, but the resulting invertase is less pure.

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* We shall refer to this as the "C" sample of invertase.

We have tried very many modifications of the above process, but with less satisfactory results.

In this manner we have made the following preparations for analysis:—

Sample D, strength ...... $\pm 0 = 33{\cdot}1'$
" E, " ...... $\pm 0 = 28{\cdot}5'$

Another sample was prepared by a slightly modified process as follows:—The first precipitation was effected with great rapidity; the heavy precipitate was dissolved in yeast liquor, and again rapidly precipitated. This precipitate was washed with 0·945 alcohol; but on account of the rapid precipitation we should expect the sample to contain yeast albuminoïd. Its activity was found to be $\pm 0 = 32{\cdot}9'$. This is sample F.

Yet another sample was prepared by precipitating the yeast liquor slowly, washing the precipitate by decantation, again dissolving in 1 part of yeast liquor, reprecipitating slowly, redissolving the precipitate, precipitating a third time, and washing as usual. The activity of this sample was $\pm 0 = 27{\cdot}9'$; it is sample G. On account of the repeated precipitations, the sample probably contained some of the products of the decomposition of invertase.

A second sample, prepared in the same way, had an activity of $\pm 0 = 33{\cdot}4'$, and it was called sample H.

The analyses of these samples will be found in Part IV, under the heading "*β-Invertan or Invertase.*"

If a preparation of active invertase is required to be kept for use when wanted, it is probably best to do so in the form of yeast liquor (see footnote, p. 874), and either use it direct or precipitate when required.

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* We have not succeeded in precipitating invertase from this solution, as any attempt in this direction renders it inactive.

Separation of the Ash.

It will be noticed that in all the preparations of invertase hitherto made there was a large amount of ash. This consisted of potassium and magnesium phosphates, and the question arose whether it was an integral part of invertase or only an impurity. It was found to be impossible to separate it from the invertase by means of precipitation with alcohol, except by many precipitations in an acid solution, and in the meantime the inverting power had quite disappeared. Recourse was therefore had to dialysis, and, as it was found that dilute hydrochloric acid had no injurious effect on invertase in solution, the dialysing solution was kept constantly acid. Each day the dialyser and its contents was weighed, and the inverting power was calculated as if nothing had dialysed out. Under these conditions the inverting power should remain a constant figure, provided there was no change in the quantity of invertase. Unfortunately these experiments were done before the influence of the presence of very minute traces of acid was understood, and this influence was intensified by the estimations being made at 54°. They are, therefore, not very regular, and one estimation is a long way out, due no doubt to a slight excess of hydrochloric acid, but on the whole they are quite near enough for the purpose in hand. The invertase preparation used contained 4·6 per cent. of water and 8·05 per cent. ash on the dry substance. 30 grams was taken = 28·6 grams dry invertase, and containing 2·3 grams ash (28·6 × ·0805). The water outside the dialyser was always found to be inactive. The organic matter and ash were estimated in it each day. The following table gives the results of the experiment:—

TABLE XXIII.—*The Separation of the Ash by Dialysis.*

Time.	Passed through dialyser.		Inverting activity of the solution calculated on the whole original substance ± 0 = .
	Organic matter.	Ash.	
1 day	0·636	0·714	54′
2 days..............	0·558	0·402	50′
3 „	0·480	0·282	65′
4 „	0·306	0·168	48′
Total 4 days	1·980	1·566	—

The invertase originally contained 2·3 grams of ash, so that 0·73 gram is left; this is equal to 2·9 per cent. on the remaining solid matter. The reduction of the ash to 2·9 per cent.[*] on the total solid matter has, in this case, had no appreciable influence on the inverting power, but it was advisable to try the effect of a still greater reduction.

With this view the experiment was repeated with the same amount of the same preparation of invertase, and the dialysis was continued for a longer time.

TABLE XXIV.—*The Separation of the Ash by Dialysis.*

Time.	Passed through dialyser.		Inverting activity of the contents of dialyser calculated on the whole of the original substance ± 0 = .
	Organic matter.	Ash.	
1 day	1·77	1·71	57′
3 days			70′
4 "	0·52	0·16	85′
5 "			78′
8 "	not weighed	—	70′
14 "			162′
15 "			104′
Total	2·29	1·87	—

The solution on the dialyser began to putrefy slightly on the 11th day, and, as it got slowly worse, it was thought useless to prolong the experiment beyond the 15th day.

An examination of the solution left on the dialyser gave the following result:—Sp. gr. = 1026·7. With a divisor of 3·85 this is equal to 6·93 grams per 100 c.c.

On estimating the ash, we found that 13 c.c. yielded 0·004 ash, so that 100 c.c. would contain 0·031 gram ash, equal to 0·45 per cent. on the solid matter. The strength was estimated, and it was found that 0·104 gram of the solution in 100 minutes gave a reading of + 5·2 div. = 9·6 T. The weight of the whole solution was 290 grams; so that, calculated in the same manner as on the previous days the strength was ± 0 = 104′.

This figure, of course, is only useful for comparison with the results obtained on previous days, it does not take into account the amount that had dialysed or that was used for experimental purposes. It is, therefore, necessary to calculate the real activity of the organic solids in the solution. This we did as follows:—The 0 point would have been reached in 132′. Now 0·104 gram of the solution contained 0·007 gram solids. Allowing for this in the usual manner, we get 9·24 minutes (0·1 : 0·007 : : 13·2 : 9·24), and multiplying this result by 7·5 to correct for the temperature of the estimation, we obtain ± 0 = 69·3′.

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[*] We shall refer to this preparation with 2·9 per cent. of ash as the "J" sample.

In passing we may state that we found the optical activity of the solid matter in the solution to be $[\alpha]_j = +55°$.*

Now in the above experiment we took a fairly active sample of invertase which had refused to part with its ash by precipitation with alcohol, and by means of dialysis with hydrochloric acid we reduced this ash from 8·05 per cent. to 0·45 per cent. on the solid matter, and that without any marked change in its inverting power. The first three days of its dialysis the activity was ± 0 = 57′, 70′, and 85′. The last day it was 69′.

We maintain that these figures show conclusively that ash does not enter into the composition of invertase.

Purification of Invertase.

It might be thought now that, having got rid of most of the ash, it would only be necessary to fractionally precipitate the invertase by means of alcohol, and then compare the several fractions to show its purity or the reverse. But here unexpected difficulties come in.

If the invertase is at all pure, it quickly loses its activity. As an instance of this we may refer to the B sample of invertase, which we stated to be the purest we succeeded in preparing. When we had examined the properties of this solution, we left it standing in a stoppered bottle for about a month, after first mixing with it sufficient weak alcohol to bring the total alcoholic strength to 0·975. At the end of the month the solution was quite clear and free from any organic precipitate, though some of the ash had crystallised. It was absolutely inactive. Weaker preparations of invertase are not so unstable, and they may sometimes be kept a long time with little injury, but anything like fractional precipitation completely destroys them, and even the inverting power of yeast-liquor itself may be destroyed by sufficiently slow precipitation.

We were not able to obtain more than slightly active precipitates from the solutions of the J and K samples of invertase after dialysis, although we tried everything we could think of to prevent the destruction of the invertase. We shall show later on that these samples must have been fairly pure mixtures of invertase with the products of its decomposition, this decomposition having been caused by the number of preliminary precipitations which the substance had undergone.

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* We shall refer to this preparation as the "K" sample of invertase.

If alcohol was added slowly to these solutions, they *milked*, that is to say, the solutions became white and opaque, exactly resembling milk. This term has been previously defined by one of us in treating of the amylans (Trans., 1882, 28). This milk was active, but if a trace of any acid was added a precipitate was thrown down which was perfectly inactive. We tried numerous experiments with the object of precipitating the invertase without destroying it; the following are typical ones:—

A. Strong alcohol was quickly added to the solution. The greater portion of it milked, but there was a small precipitate, which was tested and found to be active. Experience has shown us that a precipitate obtained thus suddenly cannot be called a fractional precipitate, and so it is useless for our purpose. It was, too, very minute. The milk was active. Nothing fell out of the solution on standing, and so it was necessary to add a drop of acetic acid to get a precipitate. The syrupy precipitate thus obtained was inactive.

B. Weaker alcohol added slowly produced no precipitate, but otherwise had the same effect.

C. We rendered the solution absolutely neutral with a little bicarbonate of soda and then added alcohol. Effect the same as in B.

D. Rendered slightly alkaline with bicarbonate of soda. Result the same as in B, but the syrupy precipitate produced by acid was slightly active. This was dried, and the activity found to be $\pm 0 = 240'$ against $70'$ of the original substance. In this case no fractionation took place, because the precipitation was effected too rapidly.

E. Rendered slightly acid (HCl). Precipitate and supernatant liquid both inactive.

F. Acidified considerably. Results the same as E.

From these experiments and many similar ones it is evident that we had come to an end of the purification in this manner; we therefore tried the effect of dialysis on a very active solution, so as to avoid the necessity of fractional precipitation after dialysis.

Here again we were defeated by the old difficulty that these comparatively pure solutions rarely retain their activity for more than a few days, and even when they appear stable, any attempt to work with them ensures their rapid destruction. Particulars of an experiment of this nature, made with sample E, are given in Part IV under the heading "Splitting up of Invertase."

We had consequently to rely on an examination of the substances in the inactive solution for a knowledge of the composition of invertase. The analysis and properties of invertase are given in detail in Part IV under the heading "*β-Invertan or Invertase.*"

Yeast Albuminoïd.

Attention must now be directed to one of the substances eliminated in the preparation of invertase. We have shown that in this process a portion of the precipitate produced by alcohol in yeast liquor is not again soluble in water (see "Separation of Invertase from Yeast Liquor"). This is the albuminoïd of yeast. In the preparation of the B sample of invertase we have shown that this precipitate amounted to 5·93 per cent. on the dry solid matter of the yeast.

Preparation.—We prepared it in the following manner:—Alcohol was added to yeast liquor until a precipitate began to form. On standing, a large, flocculent precipitate fell to the bottom. This was collected on a filter; it was found to have only a very slight invertive action. It was repeatedly washed with water, through which it diffused readily, forming a thick semi-solution, which would not pass through a filter even under pressure. In order, therefore, to separate the water, it was necessary each time of filtering to add a little alcohol, though not sufficient to throw any invertase out of solution. The albuminoïd then fell to the bottom as a well-defined, broken precipitate. When this had been done several times, the precipitate was washed with strong alcohol, pressed between blotting-paper, and dried in a vacuum over sulphuric acid. Until this final desiccation, the precipitate was almost white, but in the vacuum it rapidly assumed a dark colour. Prepared in this manner, it is a hard, brown, dull-looking mass, which is very difficult to reduce to powder.

Analysis.—We made an analysis with the following results, and for the sake of comparison we give the highest and lowest numbers obtained from the analysis of albumins (Béchamp, *Mém. Académie Scien.*, **28**, 459).

TABLE XXV.—*The Analysis of Yeast Albuminoïd compared with Albumin.*

Constituents.	Yeast albuminoïd.	Albumin.	
		Highest.	Lowest.
Carbon	54·33	55·4	49·4
Hydrogen	7·50	7·40	6·71
Nitrogen	14·88	18·83	14·60
Sulphur	none	—	none
Phosphorus	?	—	—

ımbers are calculated on the substance free from ash, which l to 3·9 per cent., consisting of potassium and magnesium 3s. Further analyses are given under the heading, "Yeast ɔïd derived from Invertase."

ies.—Precipitated yeast albuminoïd is insoluble in water, ves readily in a small quantity of caustic alkali. It is generpitated on acidifying the alkaline solution, and it falls out y if the acidified solution is placed on a dialyser till the acid d. In yeast liquor it is in an alkaline solution, but it is not ıt by acid even on boiling.

ıol is added to an alkaline solution of yeast albuminoïd, no e is formed, but the solution is converted into a milk. Exıeat, it exhales the usual smell of burning albumin, and usual black residue difficult of combustion.

ıs of yeast albuminoïd are slightly lævorotatory, but they palescent to admit of reliable readings. It is impossible, to use this property as a criterion of purity; we may state, ;hat we found the optical activity of our preparations, in ›lution, to be somewhere about $[\alpha]_j = -13°$.

!buminoïd is not precipitated by alkaline copper oxide soluth Millon's reagent, it gives no reaction in the cold, but on ıe precipitate caused by the acid turns pink.

p (*Mém. Académie Scien.*, **28**, 269) mentions an albumin separated from beer yeast; its properties were very those given above. He does not seem to have analysed it, ıd its optical activity to be $[\alpha]_j = -43·9°$.

Part IV.—The Invertan Series.

Splitting up of Invertase.

is point we have shown that practically the whole of the f yeast can be separated (*a*) from the insoluble portions of ell; (*b*) from the yeast constituents soluble in 47 per cent.) from yeast albumin; and (*d*) from ash. But when we ·ther purify the invertase, we found that on attempting to with alcohol the inverting power was destroyed, so that ; or products ceased to come within our definition of in-

ıese circumstances, we found it necessary to abandon the further purification of invertase, and to undertake in its ĸamination of the substances resulting from its altera-

ıs end in view, we turned to the K sample, which, it will be remembered, was dialysed for 15 days. We took 200 c.c. of the solution off the dialyser; this, as we have already shown, would contain 13·87 grams of solid matter. To it alcohol was slowly added; the solution became a milk, but a small, crumby precipitate was formed. This was put on one side, and, as it was too small for any practical purpose, some other small bits obtained during the fractionation were added to it, and the whole was marked "oddments."

By adding minute quantities of dilute hydrochloric acid, the milk was precipitated in three fractions. They all fell out as syrups, and the solution was eventually left perfectly clear with a slight red tinge. The 13·87 grams of solid matter was accounted for as follows. We also give the optical activity of the chief fractions:—

			$[\alpha]_j$ =
1st precipitate.........	5·6 grams	= 85 p. c.	+50·7°
2nd „	2·3 „		+55·5°
3rd „	3·85 „		+50·7°
Oddments	1·39 „	= 10 „	
Soluble in alcohol......	0·73 „		
Total	13·87		

These fractions were all obtained by actual weighings, and the moisture in each was estimated and allowed for. The exact agreement of the numbers is a satisfactory coincidence.

We may note that in dealing with the bodies of the invertan series, a mixture of any two of them is easily separated by partial precipitation with alcohol and acid, as shall be described, and we have considered a sample homogeneous when we could separate it by this means into two or more fractions, all of which had the same or nearly the same optical activity as the original substance.

It will be seen from these results that 85 per cent. of the solid matter in the dialysed solution of active invertase consisted of a syrupy substance having $[\alpha]_j$ between +50° and 56°. The 10 per cent. of oddments was a crumby substance, mainly insoluble in water. None of the fractions had any inverting power.

These three syrupy precipitates were mixed and dissolved in water to a clear solution. It was acidified, and then very carefully fractionated with alcohol. The first precipitate was very small and crumby; the second was a small, syrupy precipitate; the third and fourth contained the large bulk of the solids.

TABLE XXVI.—*The Re-fractionation of the Syrupy Precipitates.*

Precipitate.			$[\alpha]_j$.	D (divisor).*	N, per cent.
No.	Condition.	Bulk.			
1	crumby	very small	—	—	—
2	syrupy	small	—	—	4·7
3	"	large	52·4	3·85	2·21
4	"	large	54·1	3·75	2·31

There was little doubt that we were dealing with a homogeneous substance.

These experiments were repeated with the J sample of purified invertase solution described above. The results obtained were exactly similar.

It may be remarked here that the readings in the polarimeter are not very accurate for these substances, as, even when they are clear and nearly colourless, they absorb a great deal of light. Hence absolute regularity in the results is not to be expected.

All the syrupy precipitates from these two series of fractionations were mixed, and again very carefully fractionated with alcohol and hydrochloric acid.

The fractions mixed had $[\alpha]_j$ varying from +52·4° to 56·8°. The total weight was 22 grams. The mixture was divided into six fractions, which yielded the following results:—

TABLE XXVII.—*The Re-fractionation of Precipitates of Optical Activity* $[\alpha]_j = +52{\cdot}4°$ to $56{\cdot}8°$.

Fraction.	Weight.	$[\alpha]_j$.	Divisor.*	N.	C.	H.
V..........	2·5	—	—	—	—	—
W..........	3·2	56·5	3·75	2·26	—	—
X..........	5·5	53·5	3·75	—	—	—
Y..........	5·7	53·5	3·71	—	—	—
Z_1..........	1·3	53·4	3·74	—	46·5	6·82
Z_2..........	1·45	—	—	2·59	—	—
Total.......	19·65	—	—	—	—	—

It will be seen that practically no differentiation has taken place.

Fractions X, Y, and Z_1 were again mixed and fractionated with the utmost care, as follows:—

---

* Determined.

Fraction.	$[\alpha]_j$.	D.*
A. A very small precipitate........	—	—
B. A large precipitate	57·4	3·69
C. „ „	53·2	3·71
D. A very small precipitate........	—	—

From these results it would seem as if there were a slow breaking down of the substance with $[\alpha]_j + 54°$; one having a somewhat higher optical activity being amongst the products. We shall see later on that such is the case. Despite this fact, we see that we did not find it possible to differentiate the bulk of the syrupy precipitate by means of the most careful fractional precipitation with alcohol and acid, and we therefore came to the conclusion, justified by further experience, that the substance having $[\alpha]_j + 54°$ (*circa*), and which we have named *δ-invertan*, was a homogeneous compound, and that it constituted at least 85 per cent. of the products of the breaking down of invertase on precipitation with alcohol.

The only other substance found in any quantity in the dialysed solution was the crumby precipitate mentioned above, and which we have called *α-invertan*. This substance is not soluble in water or in solutions of the syrupy substance. As, however, it exists in the perfectly clear dialysed invertase solution, in company with the syrupy substance it cannot be doubted that a combination of these two formed the soluble compound, *invertase*. This is absolutely shown to be the case by the following facts:—

First. It has not been found possible to separate the two substances without destroying all inverting power. Whenever a solution of invertase is precipitated by alcohol, the total inverting power is somewhat decreased, and at the same time it is found that the precipitate is not again entirely soluble in water, thus showing that a decomposition of some kind has taken place.

Secondly. Each of these two substances may itself be decomposed by suitable means into a crumby and a syrupy substance, and *these ultimate products are identical.*

Thirdly. Between the two ultimate products we shall show that a whole series of compounds exists, of which series all the substances we have mentioned are members.

There can, then, be no doubt that invertase is a compound of the two substances which we have called α- and δ-invertan. We shall, however, give further experimental proof of this fact; and, for this purpose, we employed the very purest samples of invertase solution we found it possible to obtain.

---

* Determined.

tion of the E sample of invertase (see "Separation of In-
rom Yeast Liquor") was placed on a dialyser with a large
f hydrochloric acid. The water outside was frequently
at the end of four days the solution was nearly neutral,
y small, flocculent precipitate had fallen out. Its inverting
d optical activity were then determined and compared with
numbers before dialysis. In taking the optical activity, the
t precipitate was first filtered out.

	$[\alpha]_j$.	$\pm 0 =$
efore dialysis	+ 69·7°	28·5′
fter „	+ 54·3°	nearly inactive

e here, plainly, how difficult these nearly pure solutions of
are to work with. A treatment, which we have shown to
effect whatever on the impure samples, is in this case fatal.
l experiments have shown us that the precipitate consists
of α-invertan, which has a slight minus optical activity. No
of this with the solution having $[\alpha]_j$ + 54·3° could give an
tivity of + 69·7°; hence the two must have been in combina-
the act of separating them destroyed the invertase. There
ver, just the possibility that some substance with a higher
power may have passed through the dialyser; in order to
we have made another experiment, as, in consequence of the
portion of acid and the very small quantity of matter that
hrough, it was impossible to make any satisfactory observa-
h the diffusate.

of the solution of the G sample of invertase were taken.
cidified, and alcohol (0·870) added very slowly until a cloud
. It was then allowed to stand for two days. At the end
ime there was a large, flocculent precipitate at the bottom.
s collected and purified by mixing with water, and then
in the presence of very dilute alcohol. The washings were
the original filtrate. To the latter a large excess of strong
was added; this formed at first a milky solution, but after
two or three days it became perfectly clear, and there was
less, transparent syrup at the bottom of the beaker. We
divided the invertase solution into three portions: A, the
t precipitate; B, the syrup; and C, the alcoholic solution.
had been discarded. The alcoholic solution, as we have
ly proved under similar circumstances, contained practically
but the ash, and this was thrown away. The A fraction was
in water but soluble in alkali. It was dissolved to about
and the solution had a very faint dextrorotatory power,
g below + 1·0 division in 100 mm. It was impure α-invertan.

The B fraction was soluble in water to a colourless solution. It was dissolved in 25 c.c. of water, and in 100 mm. gave an angle of +8·3 divisions. The solution contained 6·000 grams per 100 c.c., and the $[\alpha]_j$ was therefore +53·1 It was evidently δ-invertan.

From these figures it is obvious that a mixture of A and B fractions would have had an optical activity of $[\alpha]_j =$ less than +53°. Of course neither of them had any inverting power. Comparing the factors before and after the loss of inverting power, we have

	$[\alpha]_j$.	± 0.
Before fractionation..........	+ 72·4°	27·9'
After " ....less than	+ 53·0°	none

The solid matter in the active solution had an optical activity $[\alpha]_j = +72·4°$: that of the divided, inactive fractions, taken together, less than $[\alpha]_j = +53°$; there can, consequently, be no further proof necessary that the higher optically active invertase breaks down into bodies of less optical activity, which we call α-invertan and δ-invertan.

We have already shown δ-invertan to be a homogeneous substance, and we shall, later on, show the same with regard to α-invertan; and, as 95 per cent. of the solid matter in the invertase solution was obtained in the form of these bodies (see "Splitting up of Invertase"), and as the remaining 5 per cent. was soluble in alcohol, the proof is complete that invertase yields α- and δ-invertan when an attempt is made to precipitate it.

Invertase does not always break down in the manner we have mentioned here: for sometimes other members of the series are found. α-Invertan is invariably present, but sometimes, instead of δ-invertan, either γ- or *ε-invertan* (to be described later on) takes its place. γ-Invertan we have only obtained on one occasion, and we do not know what was the cause of its appearance : but ε-invertan we have frequently found; and we believe that in this case the δ-invertan was first formed, and was then converted by the alcohol and acid into ε-invertan, as we shall, later on, show to be probable. We generally found ε-invertan when the process of purification was somewhat prolonged.

We will now take the yeast albuminoïd prepared from invertase, and then each member of the invertan series separately, giving in each case the preparation, analysis, and properties.

Yeast Albuminoïd derived from Invertase.

Preparation.—Some α-invertan, prepared from invertase in the manner already described, was dissolved in weak potassium hydroxide, and an alkaline solution of a copper salt added. At first no precipitation took place, but on adding a very large excess of strong potassium hydroxide, a large blue precipitate slowly fell out.

The solution was allowed to stand for two days, and the clear, supernatant liquid was then decanted off. We shall treat of the precipitate thus obtained under the heading "ζ-*Invertan.*"

The solution, containing everything not thrown out by copper, was acidified and precipitated with alcohol. The flocculent precipitate thus obtained was redissolved in very weak alkali and again thrown out with alcohol and acid. Finally the precipitate was redissolved in weak potassium hydroxide and an excess of acid quickly added. Nothing was thrown out of solution in this manner, so the solution was placed on a dialyser and kept there until it was perfectly neutral. This treatment caused a large, gelatinous precipitate to fall out. This was collected on a filter, dehydrated with alcohol, and dried in a vacuum. It took on much colour whilst drying.

We shall show that the substance thus obtained is very similar to the yeast albuminoïd we have already described.

Analysis.—

TABLE XXVIII.—*Analysis of Yeast Albuminoïd derived from Invertase.*

Sample.	Constituents of substance free from ash.			Ash.
	C.	H.	N.	
A............	—	—	14·61	—
B............	52·66	7·38	14·07	0·47
C............	53·79	7·19	14·17	1·00

The samples marked A and B were obtained in the manner above described. In order to test the purity of the B sample, it was redissolved in a large excess of potassium hydroxide and some Fehling's solution added. As this did not produce any precipitate, a large excess of alcohol was added. After standing two days there was a small precipitate. The clear, supernatant liquid was decanted off, and the albumin was obtained from it in the manner before described. The analysis is given above as that of the "C" sample. It will be seen that, considering that we were working with an albuminoïd, the figures agree as well as could be expected.

Properties.—The properties of this substance are, as far as we have been able to ascertain, the same as those of yeast albuminoïd.

Conclusion.—In the following table we give a comparison of the results of the analysis of the albuminoïd obtained directly from yeast and of the C sample of the albuminoïd obtained from invertase:—

TABLE XXIX.—*Comparison of the Analyses of the Albuminoïds obtained from Yeast and from Invertase.*

Source of the albuminoïd.	Constituents of substance free from ash.		
	C.	H.	N.
Invertase	53·79	7·19	14·17
Yeast.....................	54·33	7·50	14·88

These numbers agree pretty well, and leave no doubt that the substances are very similar, and although we cannot say that they are identical, we may take the mean of the two analyses as the composition of yeast albuminoïd.

$$C = 54{\cdot}06 \text{ p. c.}, H = 7{\cdot}35 \text{ p. c.}, N = 14{\cdot}53 \text{ p. c.}$$

We may note here that as this albuminoïd contains no sulphur, and, probably, no phosphorus, we have no reason for attributing to it such a large molecule as the albumins are usually considered to possess. The formula $C_9H_{15}N_2O_3$ would give

$$C = 54{\cdot}27 \text{ p. c.}, H = 7{\cdot}54 \text{ p. c.}, \text{and } N = 14{\cdot}07 \text{ p. c.}$$

Although we do not for one moment believe that the molecular weight of yeast albuminoïd is as low as this, yet we have thought it necessary to point out the possibility, because on this factor depends the molecular weight of the entire invertan series (see Part V, "Constitution of the Invertan Series").

α-Invertan.

Preparation.—We have already shown under the heading "Splitting up of Invertase," that invertase in an acid solution slowly breaks up in the presence of alcohol, with the separation of a flocculent precipitate. If this precipitate is purified by washing a few times with water and weak alcohol, and then by dialysis in the manner described in the case of yeast albuminoïd derived from invertase, *α*-invertan is obtained. In this way it is easy to prepare considerable quantities of it.

That this substance is a true compound, will be apparent from the following considerations:—We shall show that α-invertan may be split up into yeast albuminoïd and ζ-invertan. Now a mixture of these two substances containing 8·3 per cent. of nitrogen would have an optical activity of about +40°, whilst α-invertan, on the contrary, has about the same lævorotation as yeast albuminoïd.

We consider that the approximate purity of the preparation is established by the general agreement of the percentage of nitrogen contained in the three samples analysed below.

TABLE XXX.—*Analysis of α-Invertan.*

Sample.	Constituents of substance free from ash.			Ash.
	C.	H.	N.	
A............	48·03	6·65	8·35	0·70
B............	—	—	8·53	—
C............	—	—	8·15	—

The A sample analysed above was obtained by repeatedly precipitating 50 grams of the C sample of invertase with alcohol and an acid. The flocculent precipitate thus obtained was purified several times by precipitation with weak alcohol. The substance in solution we refer to under "ε-Invertan." Finally, the precipitate was dissolved in weak alkali, and a little Fehling's solution was added. A small precipitate fell out and was discarded. The α-invertan was separated from the copper solution in exactly the same manner as was described under the heading "Yeast Albuminoïd derived from Invertase." It only took on very little colour on drying. The dry substance weighed 11·5 grams.

The B and C samples were obtained in a similar manner, but in the preparation of the C sample the treatment with Fehling's solution was omitted.

It will be noticed that we have only estimated the C and H in one sample of α-invertan. The reason of this is, that in the invertan series the C and H vary with the nitrogen, only in a very much smaller degree. For practical purposes, therefore, the nitrogen alone is required. In the case of α-invertan, the nitrogen of the A sample agrees with the mean of the B and C samples, so that we take for the composition of α-invertan:—

C = 48·03 p. c., H = 6·65 p. c., N = 8·35 p. c.

Properties.—The properties of α-invertan are exactly similar to those of yeast albuminoïd, with the exception that in the presence of a very large excess of an alkali, it yields a copper precipitate as has been already described. The α-invertan is in this case split up into yeast albuminoïd and ζ-invertan; the reaction is treated of under both these headings.

For its optical activity we have obtained numbers varying between $[\alpha]_j = -11°$ and $-20°$.

β-Invertan or Invertase.

This is the substance which was primarily the subject of this investigation. We have already described our attempts to obtain it in a pure state, and we have given details of the preparation, among others, of five separate samples of which the inverting activity was found to be :—

D sample, ± 0 = 33·1′
E „ = 28·5′
F „ = 32·9′
G „ = 27·9′
H „ = 33·4′

Although these numbers do not differ very much amongst themselves, there is sufficient difference to indicate that we have not an absolutely pure body to deal with, but considering the different methods by which these samples were prepared, and the nature of the body itself, splitting up, when pure, as we have described, on the slightest handling, we are justified in concluding that we have pure invertase in our hands contaminated simply with the products of its own decomposition, a little ash, and possibly some yeast albuminoïd which has not been rendered insoluble by the single precipitation with alcohol to which the preparation has been subjected. This statement is borne out by the fact that a careful examination of several of these solutions has failed to show the presence of any substances, except members of the invertan series and ash (see "Splitting up of Invertase"). We have not used the optical activity as a test of purity, because it is not nearly such a good criterion as the inverting power. We have already given reasons for our statement that this test is the only reliable one, and that it accurately indicates the relative proportion of invertase present. We shall show later on that ± 0 = 22·5′ approximately represents the inverting activity of pure invertase, and from this factor it is easy to calculate the absolute amount of invertase present in any preparation. This would tend to show that the above samples are not sufficiently pure for analysis, were it not for the fact mentioned above that the impurity consists almost entirely of the products of the decomposition of invertase, and therefore their presence would not have a very great effect on the analysis.

Analysis.—

TABLE XXXI.—*Analysis of β-Invertan or Invertase free from Ash.*

Sample.	C.	H.	N.
D............	47·08	6·74	4·98
E............	46·64	6·70	3·92
F............	45·90	6·69	4·90
G............	46·17	6·56	3·45
H............	46·94	6·77	3·94

These members are calculated on the organic matter in the active solutions, the ash in each case being estimated and allowed for.

The strongest invertase we ever obtained was the B sample with $\pm\ 0 = 25{\cdot}1'$, but this was not analysed. Under these circumstances we adopt the mean of the E and G samples as the nearest approximation to the composition of pure invertase that we have been able to attain. We do this with the more confidence as these two samples were prepared by different methods, one of which we should expect to give more and the other less nitrogen than the true quantity, and yet they agree well with each other. The composition of invertase calculated in this way would be—

$$C = 46{\cdot}41 \text{ p. c.}, H = 6{\cdot}63 \text{ p. c.}, N = 3{\cdot}69 \text{ p. c.},$$

and this cannot be far removed from the truth.

Properties.—The action of invertase on cane-sugar is discussed in Part II of this paper.

Invertase is a white substance readily soluble in water to a clear, but somewhat viscous solution, which is not rendered turbid by boiling. The solution slowly acquires colour in contact with the air. It is insoluble in alcohol of 0·94 sp. gr., and it is, like all the series, more soluble in warm than in cold alcohol. We have already shown that it may be precipitated out of solution by alcohol with only a small percentage of loss, provided the solution is not pure. The precipitate is semi-syrupy or semi-crumby, and partakes of the colour of the mother liquor. It also takes down large quantities of all the salts in solution, from which, however, it may be partially freed by washing with 0·920 alcohol. Solutions of impure invertase submitted to careful fractionation by means of alcohol are nearly always destroyed, and so are solutions of invertase allowed to stand long in the presence of large quantities of alcohol. The purer solutions of invertase cannot be precipitated by alcohol without being destroyed, unless they are very concentrated, and a large excess of very strong alcohol is quickly added.

When invertase is precipitated by alcohol, the precipitate is never all soluble in water, showing that there is always some decomposition. Invertase will not pass through a dialyser, and, if impure, it may be dialysed for a long time without injury. It possesses no copper oxide reducing power, but readily forms with copper in alkaline solutions the characteristic copper compound described at length under a separate heading. With Millon's reagent, invertase gives no reaction in the cold, but, on heating, the solution turns a fine pink.

We have shown that it is very difficult to keep invertase, whether in solution or in the dry state, for an indefinite time, without a gradual loss of strength. We have found it best retains its power in solution (see Table I, and footnote, p. 874).

We are not able to give any definite number for the optical activity of invertase. The E sample had $[\alpha]_j = +69{\cdot}7°$ and the G sample $[\alpha]_j = +72{\cdot}4°$, whilst our strongest sample, the B sample, had $[\alpha]_j = +74°$. We think that even the highest of these figures is below the truth, as the impurities have a lower optical activity than this, the highest being δ-invertan, with $[\alpha]_j = +54°$. These figures, as well as the nitrogen estimations, bear out what we have already said of these two samples; viz., that the E sample is probably contaminated with some unprecipitated albumin, and the G sample with δ-invertan. We, therefore, take $[\alpha]_j = +80°$ as approximately representing the optical activity of invertase.

Invertase in solution is not altered by dilute mineral acids; but dilute alkalis at once destroy its activity beyond the power of recall. Lime-water does not destroy the activity if quickly neutralised.

Powdered invertase slowly and thoroughly dried in a vacuum over sulphuric acid withstands with little alteration a temperature of 100°. Two samples thus dried were placed for some hours in a current of dry air at 100° with the following results :—

	± 0 before heating.	± 0 after heating.
J sample..............	131′	174′
K „	164′	222′

The effect of heat on the inverting power of invertase solutions is peculiar, and requires a more detailed description.

Experiment A.—A solution of invertase was placed in a test-tube in a bath of cold water. The temperature was then rapidly raised. In the test-tube were a pipette and a thermometer. The solution was kept well stirred, and as the temperature rose samples was taken at intervals by means of the pipette.

Each sample, which consisted of 20 drops, about 1 gram, was placed in a cold empty beaker, and when all the samples had been collected, 25 c.c. of a 20 per cent. solution of cane-sugar was added to each. The samples all stood together for 3½ hours, and were then stopped with alkali and their optical activity observed. 4 per cent. is added to the observed angle to allow for the invertase solution.

TABLE XXXII.—*The Effect of Heat on Solutions of Invertase.*

Temperature when sample was taken.	Readings in 200 mm. tube.	Corrected readings.	Time units.
15° C.	−14·0	−14·6	20·4
35 „	−12·0	−12·5	18·7
40 „	− 6·8	− 7·1	15·6
45 „	+25·6	+26·6	6·2
50 „	+70·4	+73·2	0·4
55 „	+74·0	+77·0	0·0

Under the heading "Time Units" we give the number that corresponds in Plate I (p. 844) with the percentage of inversion calculated from the polarimeter readings. As we only require the relative numbers, and all the other conditions of experiment are the same, it is not necessary to carry the calculations any further. Bearing in mind the rule, that the amount of invertase present is in direct proportion to its inverting power, we may consider that the original amount of invertase present is represented by the number 20·4, and the other figures are in proportion to this.

We shall again refer to these results after the next experiment.

Experiment B.—In order to find out what temperature invertase can endure when heated with cane-sugar, we rapidly heated a solution of cane-sugar containing invertase, and, as the temperature rose, we took samples, and rapidly cooled them. They were all placed together in a shallow vessel of cold water, and, when they had all cooled down, the optical activity of each sample was taken. They were then allowed to stand for twenty-four hours, and at the end of that time the optical activity was again observed.

From these figures the percentage of inversion was calculated in each case, and by comparing the results with the theoretical curve of inversion (see Plate I), it was easy to find the number of time units that each reaction had passed through in the twenty-four hours. These are given in the last column of Table XXXIII. The amount of undestroyed invertase left in the samples is in proportion to the number of these time units; we have given the reasons for this in Experiment A.

TABLE XXXIII.—*The Effect of Heat on Solutions of Invertase in the Presence of Sucrose.*

Temperature reached before cooling down.	1st observation.	2nd observation.	Time units passed.
35° C.	+21·4	−11·1	26·0
55 „	+19·5	−11·3	26·2
60 „	+18·7	−11·5	26·9
65 „	+19·1	−10·6	23·4
70 „	+25·0	+ 1·6	8·9
75 „	+28·6	+28·6	0·0

These two experiments may be considered identical, except that in one case a large amount of cane-sugar was present, and in the other case none. The time of exposure to the high temperatures was no doubt not identically the same in the two experiments, but in each case as soon as the temperature reached the point named, the samples were rapidly cooled. Probably the one containing sugar, being the larger bulk, would be the longer time at the critical temperature, so this would not account for the difference in the results.

For comparison we have tabulated the results as follow:—

TABLE XXXIV.—*Showing how the Heat Resisting Power of Invertase is Affected by the Presence of Sucrose.*

Highest temperature attained.	Percentage of invertase destroyed.	
	A. Experiment (without sugar).	B. Experiment (with sugar).
15° C.	none	—
35 „	8·3	none
40 „	23·5	—
45 „	70·0	—
50 „	98·0	—
55 „	100·0	none
60 „	—	none
65 „	—	12
70 „	—	66
75 „	—	100

From this we see that invertase in solution requires a temperature fully 25° higher to destroy it when cane-sugar is present than when it is absent. In Part V of this paper we shall attempt to give an explanation of this.

For the manner in which invertase breaks down under various circumstances see heading "Splitting up of Invertase." We need only add that dry preparations seem to behave in the same way as solutions: after keeping for some time, a large portion is found to be insoluble, and the whole has lost its activity.

The inverting power of the most active invertase preparation we have ever succeeded in making was $\underset{-}{+}0 = 25{\cdot}1'$, calculated on the dry solid matter free from ash. We know that this was contaminated by the soluble products of the destruction of 12·3 per cent. of invertase. These soluble products would, we believe, amount to about 10·5 per cent. (see "Theoretical Constitution of the Invertan Series"). Making allowance for this, we have $\underset{-}{+}0 = 22{\cdot}5'$ for the activity of the remainder of the solid matter. We believe that this represents fairly well the activity of pure invertase. Our reason for this is that we have never found in the purer preparations any impurities but the products of the decomposition of invertase, ash, and sometimes a little albumin. This last, we believe, was not present in the sample we obtained these numbers from; and, as we have allowed for the other two impurities, we think ourselves justified in saying that $\underset{-}{+}0 = 22{\cdot}5'$ represents, at least approximately, the activity of pure invertase. We have shown that our purest preparations have $\underset{-}{+}0 = 25{\cdot}1'$, $27{\cdot}9'$, and $28{\cdot}5'$; the second of these was prepared from yeast liquor, quite differently from the other two. We think that these give probability to our estimations of the activity of the pure substance.

Taking this as the basis, it is easy to calculate the actual amount of invertase present in any material. In the case of yeast, for instance, from 2 to 6 per cent. of the dry solid matter would consist of invertase.

γ-*Invertan.*

Preparation.—We have only obtained this substance once, but fortunately we had enough of it to be able to prove satisfactorily its homogeneity. From a sample of invertase we obtained by careful precipitation with alcohol and hydrochloric acid two syrupy precipitates. Their optical activities were respectively $[\alpha]_j = +64°$ and $+45°$. Of the former fraction we shall treat under the heading "ε-Invertan." The 45 fraction was again carefully divided into three parts, and these were dried and powdered. Their optical activities were as follows: R, $[\alpha]_j = +67{\cdot}5°$, S, $[\alpha]_j = +47{\cdot}8°$, and T, $[\alpha]_j = +46{\cdot}0°$.

The S and T fractions were redissolved, and alcohol slowly added. The invertan nearly all fell out as a granular, syrupy precipitate, but a little was left in the solution as a milk. The precipitate was redissolved, and again treated in the same way. The two milks were added together, precipitated with acid, and the precipitate labelled Z. The main precipitate was redissolved, and weak alcohol added with great slowness. A large, flocculent precipitate gradually fell out; this was filtered off and called A. The remaining milk was fractionally precipitated in two parts, B and C. The A fraction was not soluble in water: it had the appearance of α-invertan. The remaining fractions were soluble, yielding clear solutions; their optical activities were B, $[\alpha]_j = +43{\cdot}2°$, C, $= +50{\cdot}0°$, and Z, $= +50{\cdot}4°$.

Taking all these facts into consideration, and knowing that β-, δ-, and ε-invertan break down in a similar way when precipitated by acid and alcohol, we have little hesitation in coming to the conclusion that the original precipitate obtained from the invertase, having $[\alpha]_j = +45°$, was a fairly pure substance. On attempting to purify with aci and alcohol, it slowly broke down, as do nearly all the members of this series, into two invertans, one soluble and the other insoluble in water. We have failed in attempting to prepare a further quantity of γ-invertan, and the original amount was so much reduced by the continual breaking down that we had not enough for further experiments.

The above precipitations show how completely, by careful fractionation, the members of this series may be separated from one another; and we are perfectly convinced that if the original 45 fraction had consisted, as it did eventually, of a mixture of α-invertan with δ-invertan, the first fractionation would have separated nearly all the former from the latter. We lay some stress on this point, because it applies equally to δ- and ε-invertan, both of which, as well as invertase itself, split up during purification.

Analysis.—The fraction obtained above having $[\alpha]_j = +43{\cdot}2°$ contained 0·4 per cent. of ash. The substance free from ash yielded on combustion the following numbers: C = 45·62 per cent.; H = 6·55 per cent.; N = 3·15 per cent.

Properties.—Solutions of γ-invertan are liable to split up in the manner already shown.

We have also already given all the determinations of the optical activity of this substance that we made. From these figures it is evident that it has approximately $[\alpha]_j = +45°$.

Its remaining properties it possesses in common with δ-, ε-, and ζ-invertan, and we will state them now in full, so that they need not be repeated when we describe these substances.

-Invertan is a non-crystallisable substance, easily freed from water in a current of dry air at 100°. It is soluble in all proportions in water, forming clear, colourless solutions. There is, however, a peculiar blackness about the more concentrated solutions which renders them difficult to observe in the polarimeter. The solutions are viscous, and their divisor is about 3·85; they do not cloud on boiling, and the optical activity is not altered thereby. Alcohol transforms fairly dilute neutral or alkaline solutions into a milk, which remains unaltered a long time. Acids precipitate from this a colourless syrup. By using small drops of dilute acid the substance may be fractionated in this manner. Strong solutions are immediately precipitated by strong alcohol, thus affording a means of ridding precipitates of superfluous acid, which might be injurious during desiccation. Left for any lengthened period in alcoholic solution, it assumes colour, and is liable to split up as has been described.

Even dilute solutions of γ-invertan yield the characteristic copper compound common to all the series. This is probably the copper compound of γ-invertan, as we shall show in the case of several other members of the series, that we are able to convert them into the copper compound, and then recover them without alteration. This compound is extremely difficult to purify, and it seems to have the same tendency to split up as the uncombined invertan. We have, therefore, only been able to obtain the copper compound of ζ-invertan in a pure state. We shall treat of this compound under a separate heading.

We believe we have observed that a solution of γ-invertan has the power of dissolving traces of finely-divided α-invertan, but the amounts dissolved were too small for experiment. γ-Invertan dried in thin plates becomes a glassy mass. The dried preparation keeps unaltered an indefinite time.

If a concentrated solution of the substance is allowed to stand for a long time, the invertan seems to assume a modified form. It becomes extremely viscous, and, with difficulty, miscible in water. The optical activity is not altered, and its other properties seem to be unaffected. This state appears to correspond with the meta-state of the gum acids and similar substances. It is not easy, however, to reconvert these changed bodies into the ordinary state; raising to the boiling point seems to be the most effectual plan.

With Millon's reagent, γ-invertan gives no reaction in the cold; but on heating, the solution becomes a fine pink colour.

δ-Invertan.

Preparation.—This has already been described under the heading "Splitting up of Invertase," where we also showed that it was a homogeneous substance. It is also formed by the breaking down of γ-invertan.

Analysis.—

TABLE XXXV.—*Analysis of δ-Invertan.*

Sample.	Constituents of substance free from ash.			Ash.
	C.	H.	N.	
A..............	—	—	2·31	—
B..............	—	—	2·21	—
C..............	46·5	6·82	2·59	1·4
D..............	—	—	2·26	—

The preparation of all these four samples has been described under the heading "Splitting up of Invertase." The average of the nitrogen estimations of C and D samples, the two most purified, is N = 2·43 per cent.

Properties.—Solutions of δ-invertan are liable, especially in the presence of acid alcohol, to split up into an insoluble invertan and ε-invertan. We shall give an example of this under the latter heading. The optical activity we have already shown under the heading "Splitting up of Invertase," to be about $[\alpha]_j = +54°$.

The remaining properties are given under the heading "γ-Invertan."

ε-*Invertan.*

Preparation.—If we refer back to the heading α-Invertan, we shall find that in the preparation of the A sample we broke up the invertase into α-invertan and a substance soluble in water. This latter was fractionated in three parts, N, O, and P. Their optical activity was as follows:—N, $[\alpha]_j = + 71·7°$, O $= + 64·5°$, and P $= + 65·0°$. Fractions O and P were mixed, and constitute the B sample of ε-invertan analysed below.

In the above case ε-invertan was obtained directly from invertase. We will now give an instance of its preparation from δ-invertan. This experiment was done for the purpose of obtaining some carefully purified δ-invertan, but the latter broke down during manipulation.

Several fractions of fairly pure δ-invertan were dissolved together in water, and weak alcohol was slowly added until the solution became a milk. A small precipitate fell out, which was redissolved in water and again carefully milked. The minute precipitate which fell out this time was not soluble in water, and it was discarded. The milks were all added together.

We now proceeded to fractionate this milk with the utmost care by means of minute drops of very dilute hydrochloric acid added with vigorous stirring. By this means we obtained a colourless syrup on the sides and bottom of the vessel. After standing a few hours, the milk was decanted off, and a further amount of acid added to it with the same precautions. After four fractions had been thrown out, the solution was no longer a milk, but was quite clear, and contained nothing in solution that could be thrown out by alcohol or acid. The optical activity of the four fractions was A, $[\alpha]_j = 65{\cdot}4°$, B $= 65{\cdot}8°$, C $= 65{\cdot}1°$, D $= 60{\cdot}0°$. It is evident from this that, except about one-half of the D fraction, all the δ-invertan had been converted into ϵ-invertan. The A, B, and C fractions were added together. Their united weight was 15 grams, and the mixture constitutes the C sample of ϵ-invertan.

We undertook many experiments with a view if possible to divide ϵ-invertan into fractions of different optical activity. The following is one of them:—

In the preparation of γ-invertan, the two original fractions had $[\alpha]_j = +64°$ and 45°. The former of these was dialysed with hydrochloric acid for several days; after that it was very carefully precipitated with alcohol and acid into five fractions, A, B, C, D, and E. A and E, being only very small fractions, were discarded; C also was small, and the bulk of the substance was contained in B and D. The optical activity of these two fractions was found to be B, $[\alpha]_j = +65{\cdot}4°$, and D $= +65{\cdot}9°$. Remembering that the original substance had $[\alpha]_j = +64°$, this evidence of its homogeneity may be considered complete.

It was, however, our wish still further to test the homogeneity of ϵ-invertan. With this object we undertook a long series of fractional precipitations conducted on a principle similar to that adopted by Crookes in dealing with the rare earths ("Fractionation of Yttria," *Brit. Assoc. Rep.*, 1886). To a somewhat dilute acid solution of a fairly pure ϵ-invertan, alcohol was added with great care, until a slight haze appeared in the solution; it was then allowed to stand until the next day. The fall in temperature during the night caused a considerable syrupy precipitate to separate. The mother liquor was poured off and again treated in the same manner. In this way the substance was first divided into three fractions, labelled A, B, and C. Then these were again subdivided into A_1, A_2; B_1, B_2; C_1, and C_2. The fraction A_1 was kept by itself. A_2 and B_1 were mixed; B_2 and C_1 were mixed, and C_2 was kept by itself, so that the three fractions had become four. These four were then repeatedly treated in a similar manner, until at last the number of fractions had increased to eight. The two end fractions, being very small, were discarded. The six middle ones had $[\alpha]_j = +70{\cdot}5^\circ$, $+72{\cdot}0^\circ$, $+68{\cdot}6^\circ$, $+70{\cdot}0^\circ$, $+70{\cdot}0^\circ$, and $+70{\cdot}9^\circ$. There was also considerable coloration. It is, therefore, evident that the substance is being converted into ζ-invertan, and this method is valueless as regards ε-invertan. We applied it with better results to ζ- invertan.

Analysis.—

TABLE XXXVI.—*The Analysis of ε-Invertan.*

Sample.	Constituents per cent. on substance free from ash.			Ash.
	C.	H.	N.	
A..............	44·80	6·43	2·09	1·00
B..............	44·56	6·31	2·07	0·62
C..............	44·00	6·34	2·06	0·50

We have already shown how samples B and C were prepared; the A sample was obtained in exactly the same manner as B. We have no reason to suppose that one of these is purer than the other, so we take the mean of the three as the nearest approach to the composition of ε-invertan.

C = 44·45 per cent., H = 6·36 per cent., N = 2·07 per cent.

Properties.—We have shown how the members of this series break down, especially in the presence of acid and alcohol, into two substances, one soluble and the other not. The soluble substance is generally that member of the series next below the one originally present. The insoluble one, on the other hand, contains much more nitrogen than the original substance. In the case of the splitting up of invertase, we showed this insoluble substance to be α-invertan. The insoluble substance, produced by the breaking down of δ- and ε-invertan, is exactly similar in appearance and properties to α-invertan, but from previous observations we had made we were not satisfied that it was this substance, so we made the following experiment:—

A well-purified mixture of δ- and ε-invertan with an optical activity $[\alpha]_j = +60^\circ$ was dissolved in water. It yielded a clear solution. A large excess of dilute hydrochloric acid was added, and then sufficient alcohol to cause cloudiness. It was now allowed to stand several days, a little weak alcohol being added occasionally. A

e, flocculent precipitate slowly fell out. This was filtered off
purified by repeatedly mixing with water, then throwing down
ı the weakest possible alcohol, and filtering, the washings being
ed to the original filtrate. The mixture was by this means
ded into two parts, nothing having been discarded. The por-
in the alcoholic solution was totally precipitated by strong
hol. It fell out as a colourless syrup which on examination
wed an optical activity of $[\alpha]_j = +69·8°$. The portion insoluble
ater was dehydrated and dried in a vacuum; it showed no tendency
take on colour. On combustion with copper oxide, it yielded
per cent. N.

he analysis of α-invertan showed 8·35 per cent. of nitrogen. Either,
refore, this was a different substance, or it was a mixture *of equal*
ts of α-invertan with ε- or ζ-invertan. From our experience of
comparatively small amount of difficulty of separating α-inver-
from the soluble members of the series, we should say that this
er supposition was not tenable.

n order to obtain further evidence on this point, we mixed the
dered substance with water. It swelled up into a thick jelly. A
drops of weak alkali caused immediate solution, and we were
e to take a reading in the polarimeter. The result showed a slight
tro-rotation, probably about +20°. This is about what might
xpected from the mixture above described.

he solution was then diluted, acidified, and alcohol slowly added.
soon as the precipitate showed signs of falling out, the solution
put by for a day and then filtered. The filtrate yielded with more
hol a well-marked, syrupy precipitate completely soluble in water.
insoluble portion was dried and found to contain 6·02 per cent. N.
rom these facts it may be argued that the insoluble substance was
ply a mixture of α- and ζ-invertan. We are, however, of opinion
t there are some members of the series between α- and β-invertan,
ause we think that if the soluble substance separated in the last
cipitation had been there earlier we could not have failed to have
overed it. These compounds must be very unstable, and we do
at present see any means, other than that we have employed, of
ving their existence. We believe that δ- and ε-invertan in break-
down respectively into ε- and ζ-invertan do not yield α-invertan,
some compound or compounds situated between α- and β-inver-
. These, however, being unstable substances, are soon converted
α-invertan and another member of the series containing less
ogen.

n order to test whether an invertan is split up by being converted
the copper compound, we took some of the same mixture of
nd ε-invertan ($[\alpha]_j = +60°$) which was used in the last experi-

ment, and carefully added copper sulphate dissolved in excess of ammonia and a little potassium hydroxide. The precipitate does not fall out all at once, so it was allowed to stand all night. The solution was then decanted off, acidified, and a large excess of alcohol added. There was no precipitate. The copper compound was dissolved in a little weak acid. A large excess of alcohol was added, which produced a colourless precipitate. After deducting the weight of the ash, this was found to have $[\alpha]_j = +63{\cdot}0°$, showing a gain of 3°. This is probably not more than can be justly attributed to the ordinary breaking down of the invertan, and it conclusively shows that the copper oxide combines with the δ- and ϵ-invertan, and may be again separated from them without altering them. We may add that the precipitate showed decided signs of containing some of the meta-variety of the invertans.

The optical activity of the three samples of ϵ-invertan, of which we have given the analysis, was A, $[\alpha]_j = +65{\cdot}1°$, B $= +64{\cdot}8°$, and C $= +65{\cdot}4°$. Another sample that we fractionated with great care had $[\alpha]_j = +65{\cdot}6°$. The mean of these four is $[\alpha]_j = +65{\cdot}2°$.

The remaining properties are given under the heading "γ-Invertan."

ζ-Invertan.

Preparation.—ζ-Invertan may be obtained in two ways; either by the slow breaking down of ϵ-invertan, or by the action of an alkaline solution of copper oxide on α-invertan.

As to the former method, we have already shown in the preparation of ϵ-invertan, that on attempting to purify that substance by frequent precipitations with acid alcohol, we obtained a series of fractions having an optical activity $[\alpha]_j = +70°$, or more. The ϵ-invertan being a more stable substance than either γ- or δ-invertan, this transformation is slower than in their case. We have, however, made several preparations of ζ-invertan by this means. We find the breaking down to be most rapid when the invertan is in very dilute solution, and a large excess of acid is present. When sufficient alcohol is added to form a cloud in the solution, a day's rest should be given, and then a little more alcohol added, and so on for several days.

In this manner there is no difficulty in preparing ζ-invertan from ϵ- or even δ-invertan.

The preparation of ζ-invertan from α-invertan by means of the copper compound precipitated in the presence of a very large excess of alkali has already been partly described under the heading "Yeast Albuminoïd derived from Invertase." The copper compound thus obtained was dissolved in weak acid, and purified in the usual manner, and divided into two fractions, x and y, which gave the following results:—

Fraction x .... $[\alpha]_j = +75{\cdot}5^\circ$. D = 3·95.
„ y .... $[\alpha]_j = +76{\cdot}7^\circ$. D = 4·00.

The mixture of these two fractions constitutes the sample marked G in the table of analyses.

The peculiarity of ζ-invertan prepared in this manner is that it more resembles the meta-modification than the ordinary ζ-invertan, and we have not been able to convert it into the ordinary form.

This may be due to the excessive amount of alkali which it is necesary to use. The precipitate caused by alcohol falls out rather differently, and it is not a colourless syrup, but forms a tough, white skin at the bottom of the beaker. This skin is only very slowly soluble in water. From these indications it might be thought that this is not ζ-invertan, but we are strongly opposed to this view for the following reasons. With the exception of the differences noticed above, it has the same characteristics as ordinary ζ-invertan. It has the same optical activity, and gives approximately the same numbers on combustion. It yields a copper compound under similar conditions, though this substance seems to partake slightly of its peculiarities. Lastly, we have often noticed that the conversion of any invertan into the copper compound sometimes causes it to assume the meta-form after recovery, though generally speaking the invertan is not so affected. We have, however, never seen, under other circumstances, so complete a modification as occurs in the breaking down of α-invertan. On the whole we have little doubt that this substance is ζ-invertan in the meta-form.

We have also prepared ζ-invertan from the other members of the series by converting them into the copper compound, and then freeing them from copper by dissolving in hydrochloric acid and precipitating with alcohol. As we have, however, already shown that, at least, some members of the series are not altered by this process, we think that the conversion is not due to the formation of the copper compound, but to the manipulation and fractionation which the substance undergoes. As an instance of ζ-invertan prepared in this manner directly from invertase, it will be recollected that in the preparation of the A sample of α-invertan, a small precipitate was separated by means of Fehling's solution. The invertan was recovered from this precipitate, and divided into two fractions, having R, $[\alpha]_j = +75{\cdot}0^\circ$ and S, $= +72{\cdot}0^\circ$.

The former of these constitutes the D sample, the analysis of which is given below.

We have also prepared ζ-invertan from ε-invertan by the same means, and samples E and F are from this source. These gave an optical activity of E, $[\alpha]_j$ = +78·5° and F, = 76·8°.

ζ-Invertan prepared in this manner does not, as far as we can see, differ in any way from that obtained by the slow breaking down of ε-invertan by means of alcohol and acid, though, judging by other experience, we believe it would, under some circumstances, partially assume the meta-form.

In order to thoroughly test the purity of ζ-invertan, we submitted it to the exhaustive process of fractionation we have already referred to in the preparation of ε-invertan as Crookes' method. A considerable number of fractions having $[\alpha]_j$ = + 72° – 78° were mixed, and submitted to very careful fractionation in the manner then described. We obtained in this way, by means of between 40 and 50 precipitations, 10 fractions. These were reduced to eight by discarding the very small one at each end. The others gave the following results:—A, $[\alpha]_j$ = +76·6°; B, = +75·0°; C, D, E, and F were not tested: G, = +75·5°; and H, = 73·0°. A and H were only very small fractions, and were discarded. The remaining six fractions were mixed, and again carefully fractionated into three parts. These form the samples, A, B, C, the analysis of which is given below. It was almost impossible to obtain a trustworthy reading of these fractions in the polarimeter, as they had taken on some colour, and a kind of black opalescence. However, we made out that the C sample had $[\alpha]_j$ = +73·7°, and the divisor was 3·85.

These figures leave not the slightest doubt that ζ-invertan is a homogeneous substance. They also show it to be very stable; indeed, we have only been able to alter it by boiling with sulphuric acid, and then only slowly.

Analysis.—

TABLE XXXVII.—*The Analysis of ζ-Invertan.*

Sample.	Constituents per cent. on substance free from ash.			Ash.
	C.	H.	N.	
A..............	44·74	6·38	1·55	0·50
B..............	44·45	6·13	1·50	0·40
C..............	44·76	6·26	1·84	0·38
D..............	44·98	6·49	—	0·67
E............. }	44·73	6·75	1·50	1·45
F............. }			1·68	
G..............	45·10	6·73	1·35	1·6

We have already detailed the origin of these samples. We may classify them as follows:—A, B, and C were obtained by the slow breaking down of invertase, and the intermediate products under the influence of alcohol and acid. D, E, and F were obtained from the same source by means of the copper compound. G was obtained by the same means from α-invertan, and it was in the *meta*-state. If we omit the G sample, we obtain as the mean of the others—

$$C = 44{\cdot}73 \text{ p. c.,} \qquad H = 6{\cdot}40 \text{ p. c.,} \qquad N = 1{\cdot}61 \text{ p. c.,}$$

and we take this as probably near the truth.

Properties.—Solutions of ζ-invertan are not liable to break down under any ordinary circumstances, though they slowly take on colour. Its optical activity is about $[\alpha]_j = +75°$. We have obtained numbers as low as $[\alpha]_j = +73{\cdot}6°$, and, one occasion, as high as $[\alpha]_j = +78{\cdot}7°$, but we have little doubt that the number we have mentioned is approximately correct.

The properties given under the heading γ-invertan as common to most of the soluble members of the series also apply to ζ-invertan.

Some further properties of this compound are given under separate headings, namely:—The molecular weight, the absorption spectrum, and the action of boiling sulphuric acid.

Molecular Weight of ζ-Invertan.

The three preparations of dry ζ-invertan, which were analysed under the designation A, B, and C samples, were mixed, and an attempt was made to determine the molecular weight of the mixture by means of Raoult's freezing method. We followed the details of the process as described by Auwers (*Ber.*, **21**, 712). The powdered invertan was left for 16 hours in a current of dry air at 100°. It was then dissolved in a small quantity of water, and boiled vigorously for half-an-hour. This was done to be certain of getting rid of any alcohol that the dried substance might have retained. The solution was found to contain 6·19 grams ζ-invertan per 100 c.c., equal to sp. gr. = 1023·8 (D = 3·85). The zero point of the thermometer was determined by observing the freezing point of pure water. The freezing point of the invertan solution was next twice determined. In the first experiment the depression was 0·07°, and in the second 0·06°, the mean being 0·065°.

This number calculated in the manner given by Auwers is equal to a molecular weight of 1881 $\left(19 \div \frac{96{\cdot}19 \times 0{\cdot}065}{6{\cdot}19} = 1881\right)$.

If we take into consideration the fact that there was present in the solution about 0·4 per cent. of ash, consisting principally of the acid phosphate of potash with a molecular weight of 136, we do not affect any material alteration in the number, merely increasing it to 1888. This is very much smaller than we consider probable for the compound, as we shall show under the heading "Constitution of the Invertan Series."

Absorption Spectrum of ζ-Invertan.

We have stated on several occasions that there was great difficulty with invertan solutions in obtaining readings in the polarimeter, even when the solutions were, comparatively, only slightly coloured, and clear. There is, too, a certain black look about such solutions which caused us to think that probably some well-marked absorption bands existed. We, therefore, examined the solution used in the last experiment but we did not observe any traces of a band, although a considerable portion of the violet end of the spectrum was cut off.

In view of Professor Hartley's researches, a more extended investigation of the absorption spectrum would probably yield valuable results.

Action of Boiling Sulphuric Acid on Invertan.

This reaction requires more investigation than we have been able to give it so far.

We boiled some mixed solutions of ε- and ζ-invertans of sp. gr. 1068 with 5 per cent. of strong sulphuric acid. The copper reaction slowly decreased, and on those occasions when the boiling was continued sufficiently long it disappeared altogether.

On one occasion, when about 60 grams of invertan was used, we stopped the boiling before this reaction had disappeared—1½ hours from the start. The solution was very carefully and slowly neutralised with baryta-water and filtered. Alcohol was added to the filtrate, and a precipitate was obtained having all the characteristics of the invertan series, including the copper reaction; it was purified in the usual manner. It weighed 7 grams, and was found to have $[\alpha]_j = +75{\cdot}7°$, $D = 3{\cdot}95$, and $N = 1{\cdot}05$ per cent. We shall describe this compound under the heading *η-Invertan.* The mother liquor left after the separation of this substance was evaporated in a vacuum to a syrup. The addition of 0·82 alcohol produced a further precipitate which, however, was considerably coloured. It was purified as before. It was much more soluble in alcohol than the last precipitate, and was too coloured to be read in the polarimeter. The dry substance contained 3·34 per cent. N.

The remaining solution was several times evaporated to a syrup, and taken up with dry methyl alcohol; each time there was a flocculent precipitate, but the greatest care has not enabled us to obtain a crystallisation from the methyl alcohol solution. The substance in solution constitutes a large percentage of the original invertan, and it is probably a new carbohydrate. It has a high cupric oxide reducing power. On this occasion it gave K = 84·9 and $[\alpha]_j = +10·7°$. A syrup, prepared at another time in a similar manner, gave numbers, K = 108 and $[\alpha]_j = +21°$ and $+16°$. Some ζ-invertan which we boiled with sulphuric acid until it ceased to give the copper compound yielded two substances, one soluble and the other insoluble in alcohol. The insoluble portion had an optical activity of $[\alpha]_j = +67°$, and no action whatever on Fehling's solution. The portion soluble in alcohol had $[\alpha]_j = +22·2°$ and K = 120·6; the reduction of the cupric oxide was very slow. In this case, as in every other, we completely failed to obtain any crystallisation from the reducing solution, though we took considerable pains to do so.

We are proceeding with a further study of the products of this reaction.

η-Invertan.

Preparation.—We believe this to be the first product of the action of sulphuric acid on ζ-invertan (see special heading). We have only made preliminary experiments in this direction, and have not had enough of this substance to submit it to the necessary exhaustive fractionation.

Analysis.—We have not thought it worth while to estimate more than the nitrogen, which we found in the sample under examination to be 1·05 per cent.

Properties.—Much the same as those of the rest of the series. It is readily soluble in water, and is thrown out of solution by alcohol, even when the solution is neutral. Our preparation yielded with Millon's reagent a coloration so slight that we took it to be due to impurities. It yields a copper compound, like the rest of the series.

Optical Activity.—Our sample gave $[\alpha]_j = +75·7°$, D, 3·95.

It would seem, at first sight, as if we had hardly sufficient grounds for asserting the existence of η-invertan; it might be looked upon as a mixture of ζ-invertan with some substance containing less nitrogen. Opposed to this is the fact that the substance from which we separated it contained much more nitrogen than ζ-invertan, and, more important still, such a mixture would give a vivid coloration with Millon's reagent, which was not the case. We shall show later that the existence of η-invertan might have been, and, indeed, was predicted from the constitution of the rest of the series, and that probably it is the lowest member.

We are proceeding with a further study of this substance.

Invertan Copper Compounds.

Preparation.—If an alkaline solution of copper oxide is added to a solution of any member of the invertan series, together with a sufficient excess of potassium hydroxide, a very voluminous, blue precipitate is formed. The precipitate adheres strongly together, forming a mucilaginous mass filling the whole liquid. This forms a very delicate reaction for the members of this series; but if *α*-invertan only is present, a very large excess of potassium hydroxide is required to produce the precipitate.

We have found it practically impossible to obtain this copper compound in a pure state, and we believe that several different ones exist. The voluminous precipitate carries down with it almost everything that is in the solution: and it is hopeless to try to wash it.

The freshly-precipitated invertan copper compound is, with some difficulty, soluble in water. The presence of large quantities of ammonia does not seem to decrease its solubility: but it is much less soluble in water containing potash or soda, and quite insoluble in alcohol. Hydrochloric acid immediately decomposes it, yielding copper chloride and invertan. Taking these facts into consideration, we have attempted to prepare the pure compound by the following method:—

To a weak solution of ζ-invertan a little weak Fehling's solution was added slowly, the precipitate allowed to settle, and the supernatant liquid decanted off. A little alcohol was added to the precipitate, which was then collected. It was digested in lukewarm water, in which it slowly dissolved, and was then thrown out by means of alcohol. This purification was repeated three times. A portion of the precipitate was then dried, weighed, and ignited; the ash was weighed, then boiled with water, and reweighed. The difference in weight showed 3·1 per cent. of soluble ash. For reasons given below this was looked upon as an impurity, and was deducted from the original weight of the copper compound. The remaining insoluble ash was dissolved, and the copper oxide estimated. It was thus proved that the whole of the insoluble ash was CuO; it amounted to 14 per cent. on the original copper compound after deducting the soluble ash. The percentages of CuO given below were all obtained and calculated in this manner.

The invertan copper compound was again dissolved in water and precipitated by alcohol from a very weak solution. It contained 15·0 per cent. CuO and 0·6 per cent. soluble ash. This is the smallest amount of soluble ash we have ever obtained: but we think it is small enough to render it most probable that the pure compound would contain none. The copper compound obtained in this manner contains 14—15 per cent. CuO. If the precipitate is filtered out and repeatedly redissolved in water, and reprecipitated with potassium hydroxide, it always contains a proportion of soluble ash varying from 3 to 12·4 per cent., and the CuO is also higher, 19 to 23 per cent. A precipitate obtained in this manner was dried and powdered. It contained 12·4 per cent. of soluble ash. The fine powder was digested for a long time in water, in which it is very slowly soluble. The decanted solution was always alkaline, but it was not found possible to get rid of all the soluble ash. In the end, the residue contained CuO 18·6 per cent., soluble ash 4·4 per cent.

On another occasion, an excess of sulphate of copper was added to a solution of ζ-invertan, and the compound was precipitated from the mixture by potassium hydroxide in the presence of ammonia. Ammonia has the effect of consolidating the precipitate, so that it contains less of the mother liquor. The washed precipitate was redissolved by nearly neutralising the potassium hydroxide, and then reprecipitated by fresh potassium hydroxide and ammonia. Each time the discarded solution contained less of the excess of copper, until, on the fifth purification, it was quite colourless. The final precipitate contained 21·0 per cent. CuO and 2·3 per cent. of soluble ash.

In these two last experiments the precipitates were obtained in the presence of a large excess of potassium hydroxide, and the results were, CuO = 18·6 and 21·0 per cent. We performed several other similar experiments with approximately similar results.

Some freshly-prepared copper compound containing 23 per cent. CuO and 3 per cent. soluble ash, was boiled for some time in water. The greater portion of it dissolved; the insoluble portion was found to contain CuO 32·0 per cent., and soluble ash 1·7 per cent.

It will be noticed that we have only attempted to prepare the copper compound of ζ invertan. We have already shown that at least some other members of the series yield copper compounds. On the other hand, we have proved that α-invertan is broken down on entering into the combination.

We have, however, not attempted to purify the compound of any other member of the series than ζ-invertan, because we judge that this is probably the most stable, and that the others would be even more difficult to work with satisfactorily than this one.

Constitution.—It seems probable from the above that we have obtained three distinct compounds of ζ-invertan with copper oxide, containing approximately the following amounts of CuO:—A = 14—15 per cent., B = 18·6—21·0 per cent., and C = 32·0 per cent.

Now, if the molecule of ζ-invertan contains 1 atom of nitrogen, and this is equal to about 1·6 per cent., then ζ-invertan has a molecular weight of about 875 (1400 ÷ 1·6). This, combined with CuO, would give the following percentages:—

ζ-Invertan + 1 CuO = 8·3 p. c. CuO.
„ + 2 „ = 15·4 „ (A = 14·0 – 15 p. c.).
„ + 3 „ = 21·4 „ (B = 18·6 – 21 „
(C = 32·0 p. c.).

Summary of the Invertan Series.

Before proceeding further with a consideration of the results just described, we may here conveniently summarise them.

From the purified invertase solution we have isolated a number of substances, some of them very much alike in general characteristics, but differing considerably in composition and optical activity. They may be tabulated as follows:—

TABLE XXXVIII.—*Composition of Yeast Albuminoïd and of the Invertan Series.*

Substance.	Constituents per cent. on substance free from ash.			$[\alpha]_j$ approximately.
	C.	H.	N.	
Yeast albuminoïd	54·06	7·35	14·53	−13° (?)
α-Invertan	48·03*	6·65*	8·35	−15° (?)
β- „	46·41	6·63	3·69	+80° (?)
γ- „	45·62*	6·55*	3·15*	+45
δ- „	46·50*	6·82*	2·43	+54
ε- „	44·45	6·36	2·07	+65
ζ- „	44·73	6·40	1·61	+75
η- „	—	—	1·05*	+75* (?)

The figures marked with an asterisk were obtained from the analysis of one sample only. On examining these numbers, it is to be observed to begin with that there is a great difference between the percentage of carbon in the albuminoïd and in the α-invertan; between this latter and the next member of the series the drop is smaller, and between the remaining members of the series it is irregular, due, no doubt, to the fact that we were not analysing absolutely pure substances, but still, on the whole, the decrease of carbon is apparent even here.

The same observations hold good for the percentage of hydrogen.

In ζ-invertan the carbon and hydrogen percentages closely approach a carbohydrate.

On referring to the nitrogen, we find again this diminishes from 14·53 per cent. in yeast albuminoïd to 1·05 per cent. in η-invertan. Between the albuminoïd and α-invertan there is a large drop in nitrogen; between α- and β-invertan the diminution is proportionately large; but from this downwards the decrease is gradual and steady. The decrease in each of the three constituents evidently runs in parallel lines.

From these facts the idea suggests itself that the members of the series are mixtures, in various proportions, of the albuminoïd with η-invertan, or indeed with a carbohydrate, but no other fact relating to these substances gives any support to this idea. For instance, yeast albuminoïd after being dehydrated with alcohol is not again soluble in water, whilst all the lower members of the invertan series, including η-invertan, dissolve readily to perfectly clear solutions. Then, again, α-invertan is a substance of considerable stability. It is only by treatment with strong potash and an alkaline copper solution that it can be broken up into the albuminoïd and ζ-invertan; after this treatment it is perfectly easy to separate the two products. If these substances were mixtures, the very first precipitation with alcohol of properly graduated strength would separate the albuminoïd completely; we need hardly say that such is not the case.

Let us now turn to the evidence of the optical activity. The substance with which we started, invertase or β-invertan, has a specific rotatory power of about $[\alpha]_j = +80°$. This substance, when its inverting activity is destroyed on attempting to fractionate it by treatment with alcohol, yields two bodies, the optical activity of one of which is about $[\alpha]_j = -15°$, and of the other $[\alpha]_j = +45°$, or more frequently $[\alpha]_j = +54°$. No calculation is necessary to show that no mixture of these two substances could have an activity $[\alpha]_j = +80°$. In the same way, if we use the percentage of nitrogen as a factor, it is clear that the other members of the series are not mixtures; for instance, if γ-invertan (3·15 per cent. N) was a mixture of α- and ζ-invertan, its optical activity would be $[\alpha]_j = +55°$ instead of the observed number $[\alpha]_j = +45°$. The difference between the optical activity calculated for mixtures and that observed for the lower members of the series is not so great as for those mentioned, but it is sufficiently great to be a link in the chain of evidence against their being mixtures; that they are of high stability we have shown, that their optical activities do not agree with those calculated for mixtures completes the evidence.

If we now refer back to Table XXXVIII we shall see that, with the exception of δ-invertan, we have a series of great regularity, and we feel ourselves justified in saying that between β- and ζ-invertan no member has been overlooked.

When we compare the remaining properties of the members of the series, we find that the same regularity pervades them. The one exception to this rule is the power of inverting cane-sugar; this is the property of β-invertan only.

The two stable members of the series are those at the extreme ends. The intermediate members are, as we have repeatedly shown, very liable to break down, and whenever this happens, the immediate products of the dissociation are either α-invertan or a substance nearly allied to it, and the member next below the one so dissociated. If the breaking down force acts sufficiently long, the ultimate products of the reaction are α- and ζ-invertan. Omitting α-invertan, we find that each succeeding member possesses more stability than the one above it.

All the members of the series are non-crystallisable, undialysable, and colourless. α-Invertan is insoluble in water; the others dissolve readily, forming clear but viscous solutions which do not cloud on boiling. Their divisor is about 3·85. Alkaline or neutral solutions are transformed by the gradual addition of alcohol into a milk-like fluid which passes unaltered through a filter and will not clear. This applies also to alkaline solutions of α-invertan. Acids added to the milk cause rapid precipitation. The α-invertan falls out as a large, flocculent precipitate; β- and γ-invertan are more inclined to be syrupy, whilst δ-, ε-, ζ-, and η-invertan form heavy, transparent syrups. Any of these precipitates dried in thin plates becomes a glassy mass, and, with the exception of β-invertan, the dried preparations may be kept unaltered for an indefinite period. All the members of the series yield well-defined copper compounds, but α-invertan requires to be broken up with a very large excess of potassium hydroxide.

For the other properties of the members of the series, we refer to the separate headings.

We may note here that although these compounds possess many properties in common with some of the gum acids, they, however, are in no way related to those substances, inasmuch as the ash of their *neutral solutions* is never *alkaline*.

PART V.—THEORETICAL.

Theory of Inversion by Invertase.

When we look back over the whole of the facts we have adduced with regard to the action of invertase on cane-sugar, we are forced to it that there is not much which throws light on the actual nistry of the reaction. We have, however, shown that hydrolysis nvertase is a simple chemical reaction, differing in no important icular from the ordinary chemical reactions.

rom the time curve of the reaction it is easy to make the deduc- that the invertase itself is not injured or destroyed by the act of rsion.

Te have shown that the time curve is the one that expresses hemical change "of which no condition varies excepting the inution of the changing substance." It therefore follows that the vity of the invertase does not vary during the reaction.

he same argument shows that the products of inversion have no ience on the pace of the reaction.

necessary corollary of the fact that invertase is not injured by rsion is that there is no limit to its inverting power. This we practically shown to be the case.

these respects the action of invertase on cane-sugar agrees very ely with that of boiling acids. We have little doubt that this tion would follow the same curve as the one under considera- , though we have seen no figures bearing on the point.

Table XXXIV we have shown that invertase when in the pre- e of cane-sugar will stand without injury a temperature fully higher than in its absence. This is a very striking fact, and, r as we can see, there is only one explanation of it, namely, the rtase enters into combination with the sugar. It is very difficult e how it can otherwise be explained. Further, this combination een the invertase and the sugar must last until the compound cule comes in contact with another molecule of cane-sugar, other- towards the end of the reaction, when cane-sugar is getting e, the invertase would be destroyed by the heat in the intervals een the combinations. It might be thought that our experiment he molecular weight of cane-sugar undergoing inversion would w some light on this point, but it does not throw much, because rere obliged by the conditions of experiment, to make allowance constant error in the observations, and this constant error d include the error due to the combination between the invertase sugar if it existed. It may be held, however, to show that in- se does not combine with many molecules of sugar at the same

We are not able to give further proof of the combination, h we believe to exist, between invertase and sugar, but it is us if our idea is right that the sugar must be invert-sugar, not se, otherwise if much invertase was used the optical activity of olution at the end of the reaction would not show complete sion.

We next pass to the consideration of the phenomena which we have called the residual decrease, particulars of which are given in Table VIII (p. 853).

We will briefly restate the facts. If a solution undergoing inversion is stopped with a moderate excess of a caustic alkali, the optical activity immediately drops several degrees, and then remains constant. If only a small amount of alkali is added, the drop is not sudden but gradual, taking an hour or so to accomplish, finally stopping at the same point that it would have done if much alkali had been used, and the fall in optical activity instantaneous. In one of the experiments given, this sudden drop was equal to the inversion of 23·3 per cent. of the total sugar present. We have there also shown, as is indeed obvious, that this residual decrease is not due to the action of the alkali on the sucrose. At first sight it would seem as if we had here good evidence of a gigantic combination between invertase and cane-sugar, and for some time we thought that this was the case. However, our experiment on "The Molecular Weight of Cane-Sugar undergoing Inversion" effectually disposes of this idea, because the figures obtained from observations of the freezing-point could not fail to yield well-marked indications of a combination on such a large scale, and to vary in proportion to the amount of the residual decrease. It was evident that an explanation of this very striking fact must be sought elsewhere, and it was suggested to us by Mr. A. L. Stern that the phenomenon might be due to bi-rotation of the dextrose. We have no doubt this is the case. We made several experiments on the effect of adding potassium hydroxide to solutions of bi-rotatory dextrose, and found the action similar to that which it has on solutions undergoing inversion. On one occasion, for instance, the optical activity of the dextrose dropped suddenly from $[\alpha]_j = +130°$ to $[\alpha]_j = +57$. It was shown by Brown and Morris (Trans., 1888, **53**, 614) that the freezing-point of solutions of dextrose is not affected by bi-rotation. This agrees with the fact observed by us, that in a solution of sucrose undergoing inversion, the molecular weight, before stopping, calculated from the freezing-point, is identical with the molecular weight after stopping, calculated from the optical activity. We thus see that the assumption that the nascent dextrose is bi-rotatory, explains in every particular the facts which we have observed, and which are so peculiar that they do not seem capable of any other explanation. We, therefore, think ourselves amply justified in stating that the nascent dextrose is in the bi-rotatory state; we have not been able to find any previous record of this fact, nor of the one that the bi-rotation of dextrose is instantly destroyed by potash.

About the extraordinary influence of minute traces of acidity on the reaction we have nothing definite to say. The most favourable amount of acidity is not in proportion either to the amount of a given invertase preparation present, or to the differences of temperature, yet it varies with both. Under these circumstances, it is evident that it cannot depend for its action on a chemical combination with some constituent of the invertase preparation. It would, therefore, seem as if the influence depended upon its action upon the physical state of the solution, and yet it is quite inconceivable that a difference of two parts of SO_3 per million of the solution should so alter the physical state of the solution as to change the rate of the reaction from $\pm 0 = 920'$ to $\pm 0 = 85'$ (Table XVI, p. 858). We must, therefore, leave this problem unsolved.

In conclusion we are able to state, from a consideration of the above results, that the invertase simply acts the part of a carrier of water to the sucrose, and that in doing so a loose combination is formed between the invertase and the inverted sucrose, and that the invertase is again freed from this combination in its former active state.

Constitution of the Invertan Series.

If we examine Table XXXVIII (p. 916) we shall see that, roughly speaking, the numbers obtained from analyses of the members of the invertan series are such as would be yielded by mixtures of α- and ζ-invertan. We have shown that α-invertan itself breaks down into yeast albumin and ζ-invertan.

ζ-Invertan probably splits up into η-invertan and a substance containing more nitrogen, but as we have not fully examined either of these bodies, we will for the present take ζ-invertan as the base of our calculations.

The figures we have obtained on analysis of ζ-invertan are such as may be stated in terms of yeast albumin and a carbohydrate, for if, in the figures given for ζ-invertan, we make allowance for the amount of yeast albuminoïd indicated by the nitrogen present, we obtain for the remainder the following composition :—

$$C = 43{\cdot}56 \text{ per cent.,} \qquad H = 6{\cdot}28 \text{ per cent.}$$

The theoretical hydrogen for a carbohydrate having this percentage of carbon is, $H = 6{\cdot}27$ per cent. It follows from this that the composition of the ζ-invertan may be expressed in terms of yeast albuminoïd and a carbohydrate. In order to test whether this applies to the other members of the series, and, at the same time, to find out the composition of the carbohydrate, we have allowed for the yeast albuminoïd in each member of the series, and calculated the percentage composition of the remainder. We took the nitrogen as the indication of the amount of albuminoïd present, and for its composition we used the numbers already quoted, viz.:—C = 54·06 per cent., H = 7·35 per cent., N = 14·53 per cent.

In Table XXXIX we give the results of these calculations. The last column contains the relative amounts of the carbohydrate and albuminoïd present.

TABLE XXXIX.—*Composition of the Carbohydrate after allowing for the Albuminoïd.*

Member of series.	Constituents of the carbohydrate.		Parts of the carbohydrate to 1 of yeast albuminoïd.
	C.	H.	
α-Invertan	40·00*	5·70*	0·74
β- "	43·81	6·38	2·94
γ- "	42·95*	6·33*	3·61
δ- "	44·98*	6·71*	5·00
ε- "	42·85	6·20	6·02
ζ- "	43·56	6·28	8·08
η- "	—	—	12·84

In comparing these figures it must be remembered that all the errors both of preparation and analysis are thrown on to these results, and very close agreement cannot therefore be expected.

We calculate the mean of these figures by first averaging those marked with an asterisk, and which were obtained from only one sample, we thus get C = 42·64 and H = 6·25 per cent. We again average these with the other members, and obtain C = 43·22 and H = 6·28 per cent. The theoretical hydrogen for a carbohydrate having this amount of carbon is H = 6·31 per cent., a number practically identical with that obtained.

These numbers would seem to prove that the composition of this hypothetical carbohydrate comes between an "*in*" and an "*on*" body.

In carbohydrate .... C = 44·44 per cent., H = 6·17 per cent.
Invertan carbohydrate C = 43·22 " H = 6·28 "
On carbohydrate ..... C = 42·11 " H = 6·43 "

Although we have thus shown that the figures we have obtained for members of this series are such as might approximately be obtained from certain mixtures of yeast albuminoïd with a carbohydrate of the above composition, yet at present we do not believe that the substances in question do directly combine to form the series. Our reasons are as follows:—If we turn back to our description of the individual members of the series, we shall find that η-invertan alone of the series gives little or no indication of albumin when tested by Millon's reagent. Of course we cannot say for certain that our sample was η-invertan, but we shall show directly that such a substance probably exists, and such being the case, we think it must be admitted, on referring to our description, that the substance we obtained was most probably η-invertan. Now from this behaviour with Millon's reagent we are led to believe that if albumin is present in η-invertan, it is in much closer combination than in ζ-invertan and the other members, and therefore we prefer to take η-invertan and not the hypothetical carbohydrate as the base of this series of compounds.

We regard the members of the invertan series as compounds of yeast albuminoïd with η-invertan. Taking this hypothesis as a standpoint, it will be possible to form some idea of the manner in which the series is built up, but it will first be necessary to attribute an approximate composition to η-invertan. This is not difficult to do if we place it immediately below ζ-invertan in the regular series. In this way we attribute to it approximately the composition AS_{18}, where A represents 1 part by weight of yeast albuminoïd, and S, 1 part by weight of the carbohydrate.

We have found some difficulty in attempting to convey our ideas of the proximate constitution of the invertan series. This is mainly due to the fact that we have no data to enable us to attribute a molecular weight to the albuminoïd; hence, we have been obliged to employ parts by weight to represent the constitution instead of the usual molecular formulæ.

We next turn to α-invertan. The composition of this substance is approximately A_4S_3, that is to say, 7 parts by weight of α-invertan contains 4 parts of yeast albuminoïd and 3 of the hypothetical carbohydrate.

The other members are formed by the union of these two substances according to the general formula $\eta + \alpha_n$, where η represents three times η-invertan ($3AS_{18}$), and α, α-invertan (A_4S_3). It will be noticed that the symbol η represents 57 parts by weight, whilst α represents 7.

A homologous series is thus formed, each member differing from the one below it by α.

According to this idea, β-invertan would be $\eta\alpha_5$, that is to say, its composition is 57 parts by weight of η-invertan + 35 (7 × 5) parts by weight of α-invertan, making a total of 92 parts of β-invertan, of which 23 are albuminoid and 69 the hypothetical carbohydrate. γ-Invertan, in like manner, is $\eta\alpha_4$, so that 85 parts by weight would contain 57 parts of η-invertan and 28 (7 × 4) of α-invertan, which is equivalent to 19 parts of albuminoid and 66 of carbohydrate.

According to this theory, the constitution and composition of the members of the invertan series are as follows:—

TABLE XL.—*Hypothetical Composition and Constitution of the Invertan Series.*

Name of substance.	Constitution.	Composition, parts by weight.	Ultimate composition.		
			C.	H.	N.
α-Invertan	α	A_4S_3	49·41	6·90	8·30
β- ,, ...	$\eta\alpha_5$	$A_{23}S_{69}$	45·93	6·57	3·63
γ- ,, ...	$\eta\alpha_4$	$A_{19}S_{66}$	45·64	6·54	3·25
δ- ,, ...	$\eta\alpha_3$	$A_{15}S_{63}$	45·30	6·51	2·79
ε- ,, ...	$\eta\alpha_2$	$A_{11}S_{60}$	44·90	6·47	2·25
ζ- ,, ...	$\eta\alpha_1$	A_7S_{57}	44·40	6·42	1·59
η- ,, ...	η	A_3S_{54}	43·78	6·36	0·76

A represents 1 part by weight of albumin and S, 1 part by weight of the carbohydrate. We have made the calculations on the following percentage composition:—

A .... C = 54·06 p. c., H = 7·35 p. c., N = 14·53 p. c.
S .... C = 43·22 ,, H = 6·28 ,,

The carbon and hydrogen determinations (*v.* Table XXXVIII) agree as well with these theoretical numbers as could be expected when dealing with this class of bodies, and when we look at the numbers obtained for the nitrogen and compare them with the theoretical ones, we find the agreement very close indeed.

Now let us see what happens when active invertase breaks down during purification. The first reaction is expressed by the formula

$$\eta\alpha_5 = \eta\alpha_4 + \alpha$$

or more usually

$$\eta\alpha_5 = \eta\alpha_3 + 2\alpha.$$

The latter formula represents the splitting up of invertase into α- and δ-invertan, and bearing in mind the relative parts by weight represented by η and α, we see that 92 parts of β-invertan have split up into 78 parts of δ-invertan and 14 parts of α-invertan.

The δ-invertan, again, is destroyed by the action of acid and alcohol, breaking off of 7 parts by weight of α-invertan at a time, and being degraded successively to ε-, ζ-, and, perhaps, if the conditions are favourable, to η-invertan.

The α-invertan which is formed may be divided by means of the copper compound into ζ-invertan and albumin, $6A_4S = \eta + 23A$. This reaction involves a more complete splitting up into component parts than any of the others, and we have shown that it is only effected in the presence of very strong alkali.

It will be seen from Table XL that the existence of η-invertan, the last of the series, is rendered probable by the numbers obtained on analysis of the remainder of the series, and this, combined with the single impure sample we have obtained of this substance, leaves little doubt in our minds that we shall be able to prepare it in larger quantities.

We will now compare the numbers obtained for the molecular weight of ζ-invertan with the probable molecular weight if our hypothesis is correct.

It will be remembered that when speaking of the copper compound of ζ-invertan we calculated roughly that the molecular weight of the latter substance would be 875 or some multiple of that number. If we refer to Table XL, we shall see that according to our hypothesis ζ-invertan must contain at the very least 2 molecules of the albuminoïd, whilst it probably contains more. We have already shown (heading "Yeast Albuminoïd derived from Invertase") that yeast albuminoïd may possibly have a molecular weight as low as 199, so that in ζ-invertan the molecular weight of the albuminoïd portion must, at the very least, be 398. In Table XXXIX we have further shown that ζ-invertan contains 8·08 times as much carbohydrate as it does albuminoïd. This gives us a total molecular weight of 3614 ((398 × 8·08) + 398). This number, then, 3614, is the lowest possible molecular weight of ζ-invertan if our theory of the constitution of the invertan series is even approximately correct, unless, indeed, we take ζ-invertan instead of η- as the base of the series, under which circumstances the above figures, 3614, might be halved, but in all probability the molecular weight of ζ-invertan is very much higher than this figure. It, however, agrees fairly well with the quadruple of the number given above ($875 \times 4 = 3500$). With regard to the number obtained from the estimation of the molecular weight by Raoult's method, which it will be remembered was 1888, this again is too low, though it approximates closely to one half of the least possible number ($3614 \div 2 = 1807$). Under these circumstances we must say that although the evidence obtained from Raoult's freezing method is opposed to our hypothesis of the constitution of the invertan series, we do not attribute much importance to the fact.

In conclusion, we wish to state that although we have been at some pains to point out in what simple manner a hypothetical series of combinations could be formed so as to satisfy all the requirements of the ascertained facts, we do not for one moment think that the series really is built up in exactly the way we have indicated. At the same time we fully believe that the invertan series will eventually be found to be formed in a manner in many points closely resembling our hypothesis, and we hold that for the present it will be convenient to look upon this as a good working theory. We consider we have advanced the knowledge of the subject a stage, and arrived at a position at which a record should be made; this we have done. We hope that a further study of the bodies we have only imperfectly described, either by ourselves or other workers, will lead to results as interesting and important as are foreshadowed in this paper.

PART VI.—SUMMARY.

The following is a short summary of the principal results of our work, arranged as much as possible in the same order as has been observed in the body of the paper:—

1. The rate of inversion of cane-sugar by means of invertase may always be expressed by a definite time-curve; this curve is practically that given by Harcourt as being the one expressing a chemical change "of which no condition varies, excepting the diminution of the changing substance." Whatever the conditions may be under which inversion is taking place, as long as these conditions remain unchanged, this curve is adhered to. There are, however, some slight, but apparently constant, deviations from the theoretical curve.

2. When the degree of acidity is that most favourable for the action of invertase, the rapidity of the action is in proportion to the amount of invertase present.

3. The most favourable concentration of the sugar solution at a temperature of 54° is about 20 per cent. Below that, there is a rapid decline in the speed of inversion. Greater concentrations are only slightly less favourable until about 40 grams per 100 c.c. is reached. In saturated solutions inversion only proceeds with extreme slowness.

4. The speed of inversion increases rapidly with the temperature until 55—60° is reached. At 65°, the invertase is slowly destroyed,

and at 75°, it is immediately destroyed. At the lower temperatures, the speed of the action increases with rise of temperature in accordance with Harcourt's law, the rate being about doubled for 10° rise, but above 30° the increase is not nearly as rapid. Elevated temperatures have no permanent effect on the activity of invertase, so long as they are not sufficiently high to destroy it.

5. The caustic alkalis, even in very small proportions, are instantly and irretrievably destructive of invertase.

6. Minute quantities of sulphuric acid are exceedingly favourable to the action, but a slight increase of acidity beyond the most favourable point is very detrimental. The most favourable amount of acid increases to some extent with the proportion of invertase, and decreases with rise of temperature, but we have not been able to discover on what it depends. We find that in studying the action of invertase, it is of the utmost importance that the most favourable amount of acid should be employed, otherwise correct results cannot be obtained. At a temperature of 60°, the action is almost stopped, unless exactly the right amount of acid is used, whilst if this factor is properly adjusted, inversion proceeds at (probably) the maximum speed.

7. The influence of alcohol varies in direct proportion with the amount present. 5 per cent. of alcohol decreases the speed of the action by about one half.

8. The dextrose formed by the action of invertase is initially in the birotary state, and, therefore, the optical activity of a solution undergoing inversion is no guide to the amount of inversion that has taken place.

9. If a caustic alkali be added to a solution undergoing inversion, and the optical activity be allowed sufficient time to become constant, it is a true indicator of the amount of inversion that had taken place at the moment of adding the alkali.

10. A sample of invertase which had induced inversion of 100,000 times its own weight of cane-sugar was still active; and we have shown that invertase itself is not injured or destroyed by its action on cane-sugar. Under these circumstances there is evidently no limit to the amount of sugar which can be hydrolysed by a given amount of invertase.

11. The inversion of cane-sugar by means of invertase is a simple chemical change, differing in no important way from those which inorganic substances undergo.

12. The products of inversion have no influence on the rate of the action.

13. A solution of invertase will withstand a temperature 25° higher in the presence of cane-sugar than in its absence. From this fact we

are of opinion that when invertase hydrolyses cane-sugar, combination takes place between the two substances, and the invertase remains in combination with the invert-sugar. The combination breaks up in the presence of molecules of cane-sugar.

14. A means of estimating the activity of a material containing invertase has been devised; the result is recorded by means of the time factor, $\pm 0 = x$ min. In this equation, $\pm 0 =$ a certain definite amount of work, and $x =$ the time necessary to perform it. The expression means that the given inverting material takes x minutes to invert a standard amount of cane-sugar under standard conditions. The number x varies in inverse proportion to the actual amount of invertase contained in the material or materials under examination.

15. If sound brewer's yeast be pressed, and then kept at the ordinary temperature for a month or two, it does not undergo putrefaction, but changes into a heavy, yellow liquid. The product possesses no power of fermentation, but an apparent increase takes place in the inverting power.

16. From such liquefied yeast, it is easy to filter off a clear solution of high hydrolytic power; and we have shown that all the invertase of the yeast is in this solution. We have named it "yeast liquor," and it has a specific gravity of about 1080. It will remain for a long time unaltered, excepting that the colour darkens. If exposed to the air it may slowly become covered with mould.

17. If spirit be added to yeast liquor until the mixture contains 47 per cent. of alcohol, the whole of the invertase separates with only a slight loss of power. This precipitated invertase may be washed with spirit of the same strength and then the residue either dehydrated with strong alcohol and dried *in vacuo*, or else it may be extracted by means of 10 to 20 per cent. alcohol and then filtered. The filtrate contains the invertase. On one occasion the extent of the loss involved by this process was determined and it was found that all the invertase of the yeast liquor was present in the filtrate except 12·3 per cent.

18. We have not been successful in further purifying invertase preparations carefully made in this manner, as the slightest attempt at purification destroys the invertase. We have succeeded in preparing invertase almost free from ash.

19. The inverting power of pressed English yeast varies from $\pm 0 = 1000'$ to $\pm 0 = \pm 3000'$; this is equivalent to about $\frac{1}{3}$ of these numbers on the dry solid matter of the yeast.

20. The inverting power of the most active invertase preparation made was $\pm 0 = 25{\cdot}1'$ on the dry solid matter. We believe that pure invertase would approximately have $\pm 0 = 22{\cdot}5'$.

21. The dry solid matter of yeast contains from 2 to 6 per cent. of invertase. 5·8 per cent. of invertase was separated from one sample of yeast.

22. During the preparation of invertase from yeast liquor an albuminoïd is obtained, which is not redissolved by water. This is termed yeast albuminoïd, and it possesses all the characteristics of an albuminoïd.

23. Invertase when it approaches a pure state is a very unstable substance. The products of its decomposition have been carefully examined and are found to constitute a new series of substances belonging to *the invertan series.*

24. The invertan series is a homologous series of substances which on analysis yield numbers which may be expressed in terms of an albuminoïd and a carbohydrate. Seven members of the series are described.

25. We consider that invertase itself is a member of the invertan series, and call it β-invertan. If the products of its decomposition are examined, it is usually found that they consist of α- and δ-invertan. The former contains more, and the latter less, nitrogen than invertase.

26. α-Invertan is insoluble in water, and in all its other properties seems to resemble yeast albuminoïd. It contains 8·35 per cent. N. It is a very stable substance.

27. β-Invertan or invertase is soluble in water, and is the only member of the series which has the power of inverting cane-sugar. It contains about 3·69 per cent. N, and its optical activity is $[\alpha]_j = + 80°$ (?).

28. γ- and δ-Invertan are products of the splitting up of invertase. One or other of these two substances seems invariably to be formed. They both contain less nitrogen than invertase, and are always accompanied by α-invertan. Both are readily soluble in water. They contain respectively 3·15 and 2·43 per cent. N, and their optical activity is $[\alpha]_j = + 45°$ and $+ 54°$.

29. ϵ-Invertan is formed from the slow breaking down of δ-invertan. At the same time an insoluble substance, resembling α-invertan, is formed. This probably consists of an unstable member of the series coming between α- and β-invertan. ϵ-Invertan is soluble in water, and has $[\alpha]_j = + 65°$. It contains 2·07 per cent. N.

30. ζ-Invertan results from the splitting up of ϵ-invertan in the same way that the latter is formed from δ-invertan. Its optical activity is $[\alpha]_j = + 75°$, and it yields 1·61 per cent. N.

31. η-Invertan is formed by the action of boiling sulphuric acid on ζ-invertan. It contains less nitrogen than the latter substance, but the substance has not yet been sufficiently investigated to give reliable figures.

32. The further products of the action of sulphuric acid on ζ-invertan are two soluble substances, one containing a considerable amount of nitrogen, and the other with little or no nitrogen, a high cupric reducing power and a low (dextrorotatory) optical activity.

33. The properties of all the members of the series, except α-invertan, are very similar. They are all soluble in water, forming clear solutions, which do not cloud on boiling. They are all readily thrown out of solution by alcohol, provided a little acid is present; the precipitates so formed are transparent, colourless syrups, soluble in water in all proportions. The solutions are all dextrorotatory.

34. All the members of the invertan series, except η-invertan, yield a pink coloration on boiling with Millon's reagent.

35. All the members of the invertan series, except α-invertan, when submitted to the action of an alkaline copper solution, readily yield a very characteristic copper compound, from which the invertan (except β-invertan) may be separated unaltered. Invertan can probably form several such copper compounds, all having a similar appearance, but affording different percentages of copper oxide.

36. In the presence of a very large excess of alkali, a copper compound is also formed from α-invertan, but on examination it is found that the α-invertan has been split up into an albuminoïd and ζ-invertan, the copper compound being that of ζ-invertan.

37. We believe that the members of the invertan series are combinations of yeast albuminoïd with η-invertan, and that η-invertan is probably a combination of yeast albuminoïd with a carbohydrate. According to this theory, the composition of the carbohydrate present in the invertan series, calculated from the average of all the analyses, would be C = 43·22 per cent. and H = 6·28 per cent. These numbers agree very closely with those required by a hypothetical carbohydrate, coming midway between the *in* and the *on* groups.

38. We find that η-invertan contains 18 parts by weight of this carbohydrate to 1 of albuminoïd, and that α-invertan contains 3 parts of the carbohydrate to 4 of albuminoïd. The other members of the series are formed by the union of these two substances according to the general formula $\eta + \alpha_n$, where η represents η-invertan, and α represents α-invertan. In this way, we look upon invertase (β-invertan) as $\eta\alpha_5$. This splits up into α- and γ-invertan, according to the formula $\eta\alpha_5 = \eta\alpha_4 + \alpha$. $\eta\alpha_4$ represents γ-invertan, and this may be further transformed, by the elimination of α, into $\eta\alpha_3$-, δ-invertan.

39. The numbers calculated for the constitution of the above theoretical homologous series agree with considerable closeness with those obtained from the analysis of members of the invertan series.

40. The number obtained from a single determination by Raoult's freezing process for the molecular weight of ζ-invertan is considerably less than the possible molecular weight of ζ-invertan according to our theory of its constitution.

LXI.—*Contributions to the Knowledge of Mucic Acid.* Part II. *Action of Phosphorus Pentachloride on Mucic Acid.*

By S. Ruhemann, Ph.D., M.A., and W. J. Elliott, B.A.

The small yield of dichloromuconic acid formed by the action of phosphorus pentachloride on mucic acid induced us to investigate this reaction more closely, with the view of isolating and studying the other substances produced along with the above-mentioned compound. This inquiry led to the discovery of a new acid, isomeric with that described by Bode (*Annalen*, **132**, 95).

A mixture of mucic acid and phosphorus pentachloride in the proportions given by this chemist was warmed in a paraffin-bath to a temperature of 120°, and the product gradually poured into water and allowed to cool. The filtrate from the dichloromuconic acid which had crystallised out, contains a further quantity of this acid, which Bode extracts by neutralising the solution with lime and adding hydrochloric acid to the concentrated filtrate. In this last operation we deviated from Bode's directions.

The original filtrate from the dichloromuconic acid was frequently shaken with ether until the latter remained almost colourless. On distilling off the solvent, a yellowish-red oil of peculiar odour was left, which after standing for several hours over sulphuric acid solidified to a mass of crystals. These are readily taken up by water, with the exception of a portion of the sparingly soluble dichloromuconic acid. The aqueous solution when distilled with steam yields a light yellow oil, possessing the characteristic pungent odour which was noticed with the ethereal extract. The small quantity of this substance which we obtained has prevented us from examining it further.

The remaining aqueous solution was again extracted with ether, and after removal of the latter a dark-coloured product was left, which still contained some dichloromuconic acid. For its purification we made use of an observation that the new acid, contained in the ethereal extract, though very readily taken up by water, is soluble with difficulty in concentrated hydrochloric acid. The residue obtained after evaporating the ether was dissolved in water, and the solution saturated with hydrogen chloride, when a dark-coloured, crystalline precipitate was thrown down, which was collected and washed with hydrochloric acid. The red aqueous solution of these crystals was boiled with animal charcoal, and the pale yellow filtrate shaken with ether. On distilling off the ether, almost colourless needles of the new compound were obtained. The various filtrates were subjected to the same treatment and yielded more of the acid.

The operation of throwing down the acid from the aqueous solution of the ethereal extract by hydrochloric acid seems to be necessary for its purification, if the product has not been previously treated with steam for the removal of the pungent oil, otherwise the latter adheres to the acid.

This new substance, which we call *β-dichloromuconic* acid to distinguish it from Bode's (α-) dichloromuconic acid, melts at 189°, whilst the latter sublimes at 260° with partial decomposition, without melting (C. J. Bell, *Berichte*, 12, 1271). The β-acid is, as mentioned before, very readily taken up by water, so readily, in fact, that one can hardly use this solvent for its crystallisation; the α-acid, on the other hand, is only sparingly soluble in cold water. Ether dissolves the new acid with the greatest facility, whilst Bode's acid is not easily taken up by this solvent. β-Dichloromuconic acid is, as stated before, only sparingly soluble in cold hydrochloric acid, but it dissolves on boiling, and crystallises out in needles on cooling. This property can be used for its final purification.

The analysis of this compound recrystallised from hydrochloric acid and dried at 100° gave numbers corresponding with the formula $C_6H_4Cl_2O_4$:—

	Theory.	Found. I.	Found. II.
C	34·12	34·23	—
H	1·90	2·05	—
Cl	33·64	—	33·81

To prove that this acid is a dicarboxylic acid, we determined its basicity, and obtained the following result:—For neutralisation of 0·242 gram of β-dichloromuconic acid a volume of titrated potash solution containing 0·1289 gram of KHO was required; this corresponds to 53·26 per cent. of acid, the calculated percentage being 53·08.

Barium β-Dichloromuconate.—The salts of β-dichloromuconic acid with the alkalis and alkaline earth metals are very soluble in water.

the latter, we have only examined the barium compound. This s prepared by neutralising the acid with baryta, and adding alcohol the concentrated solution, when a slightly coloured precipitate was own down, which dried over sulphuric acid has the composition $H_2Cl_2O_4Ba + H_2O$:—

	Theory.	Found.
Ba	37·63	37·96

This salt, on drying at 100°, loses only ½ mol. H_2O, as indicated by following analyses of two different preparations:—

	Theory for $C_6H_2Cl_2O_4Ba + \frac{1}{2}H_2O$.	Found.		
		I.	II.	III.
Ba	38·48	38·35	38·5	38·4

The rest of the water does not go off completely before 160°; at s temperature it loses 2·41 per cent., the calculated percentage (for nol. of H_2O) being 2·53. The barium determination of this sample responds with the formula $C_6H_2Cl_2O_4Ba$:—

	Calculated.	Found.
Ba	39·60	39·83

Lead acetate when added to an aqueous solution of the acid proces a white precipitate of *lead β-dichloromuconate*, which when ed at 100° contains 1 mol. H_2O. The formula $C_6H_2Cl_2O_4Pb + H_2O$ uires:—

	Theory.	Found.	
		I.	II.
Pb	47·695	47·53	47·83

This salt does not lose its water of crystallisation completely below)°, and decomposes if heated a few degrees above that temature.

Silver nitrate added to the solution of the acid neutralised with monia precipitates a white silver salt, which when heated in a cible suddenly decomposes, throwing a black voluminous mass out the vessel. This behaviour prevented us from determining the ount of silver in the salt.

Monethyl β-Dichloromuconate.—The action of hydrogen chloride on a ation of the acid in absolute alcohol gives rise to the formation of mono- and di-ethyl salts of β-dichloromuconic acid. The alcoholic ation, saturated with the gas, was allowed to stand for 12 hours, l then poured into water. The oil which separated was taken up ether, and on distilling off the solvent a yellow oil was left, which partially solidified when exposed over sulphuric acid in a vacuum. The crystalline product freed from the oil by pressure is extremely soluble in ether and in alcohol, and comes down from these solvents in the form of an oil which solidifies after some time. The substance is also soluble in cold water, more readily in boiling; the aqueous solution, which has a strongly acid reaction to litmus paper, becomes milky on cooling, and deposits colourless prisms which soften at 100° and melt at 109—110°. On analysis, numbers were obtained which correspond with the formula of the acid ethyl salt of β-dichloromuconic acid, $C_6H_3Cl_2O_4(C_2H_5)$.

	Theory for $C_8H_8Cl_2O_4$.	Found.	
		I.	II.
C..............	40·17	39·71	40·10
H..............	3·347	3·54	3·49

This compound is easily dissolved by alkalis, and the salts thus formed are very soluble in water; they were not further studied.

The action of ammonia on the organic salt gives rise to the formation of *β-dichloromuconamic acid.* A solution of the monethyl salt of the acid in alcohol when saturated with ammonia gas deposits crystals which are, no doubt, the ammonium salt of β-dichloromuconamic acid. The salt, however, readily dissociates into ammonia and the acid. The latter is taken up by water with the greatest facility, and crystallises from it in microscopic needles, which are only sparingly soluble in alcohol and decompose at 200°.

The composition of this acid was fixed by a nitrogen determination. The formula $CONH_2 \cdot C_4H_2Cl_2 \cdot COOH$ requires:—

	Calculated for $C_6H_5Cl_2NO_3$.	Found.
N................	6·67	6·89

Lead acetate, as well as silver nitrate, when added to aqueous solutions of the nitrogenous acid produced white, gelatinous precipitates of the corresponding salts.

Diethyl β-Dichloromuconate.—In order to effect a complete separation of the monethyl salt from the oil formed along with it by the action of hydrogen chloride on β-dichloromuconic acid dissolved in alcohol, we proceeded in the following manner. The ethereal solution of the etherification-product of the acid was shaken with dilute sodium carbonate, and the aqueous layer separated and acidified with sulphuric acid, when the acid salt was precipitated. This was taken up by ether, and on evaporating the solvent the previously described substance was left.

The ethereal layer from the treatment with sodium carbonate, after removal of the ether, yielded a light yellow oil, which had a pleasant odour, distilled at 195—196° under a pressure of 60 mm., and did not solidify in a freezing mixture. Analysis showed that this oil was the diethyl salt of β-dichloromuconic acid. The formula $C_6H_2Cl_2O_4(C_2H_5)_2$ requires:—

	Theory for $C_{10}H_{12}Cl_2O_4$.	Found.
C	44·94	44·60
H	4·49	4·39

β-Dichloromuconamide.—Aqueous ammonia when added to the diethyl salt dissolves it after a short time, and the solution deposits a white solid which is very soluble in alcohol, slightly in cold water, readily in boiling water, and crystallises from it in silky needles melting at 232° with decomposition.

On analysis, results were obtained which correspond with the formula $CONH_2{\cdot}C_4H_2Cl_2{\cdot}CONH_2$:—

	Calculated for $C_6H_6Cl_2N_2O_2$.	Found. I.	Found. II.
C	34·45	34·80	—
H	2·87	2·94	—
N	13·40	—	13·62

The differences in the physical properties which these acids, Bode's (α-) acid and β-dichloromuconic acid, exhibit are also found in their derivatives: The diethyl salt of the α-acid is a solid which melts at 96° (Wichelhaus, *Annalen*, **135**, 251; Bell, *Berichte*, **12**, 1273), the corresponding derivative of the other (β-), a liquid which does not solidify in a freezing mixture of ice and salt; again, the amide of α-dichloromuconic acid is insoluble in water, sparingly soluble in alcohol, decomposing at 250° (Ruhemann and Blackman, Trans., 1890, 370); the amide of the β-acid, on the other hand, is readily soluble, both in alcohol and in water, and melts at 232°.

The formation of both ethereal salts from β-dichloromuconic acid rendered it desirable to rèinvestigate the action of hydrogen chloride on the alcoholic solution of the α-acid, in order to determine whether in this case also both the ethyl salts are produced. On applying the same method as described above for the separation of the two salts of the β-acid, it was found that sodium carbonate extracted from the ethereal solution of the etherification-product, besides some unaltered acid, a very small quantity of a compound which, when boiled with water, melted and then entered into solution. On cooling, colourless plates crystallised out which melted at 135°, and were probably the monethyl salt of α-dichloromuconic acid, but the amount of substance formed was not sufficient to verify it by analysis.

Action of Reducing Agents on β-Dichloromuconic Acid.

α-Dichloromuconic acid is, as Bode (*loc. cit.*) found, reduced by sodium amalgam to hydromuconic acid (m. p. 195°), which, according to the recent researches of v. Baeyer and Rupe (*Annalen*, **256**, 1) has the constitution $COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH$. They further showed that this acid, which they call Δ^{β}-hydromuconic acid, is on boiling with sodium hydroxide transformed into its isomeride, namely, $\Delta^{\alpha\beta}$-hydromuconic acid (m. p. 168—169°),

$$COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

and that, therefore, the former acid is to be regarded as the original reduction-product of Bode's dichloromuconic acid.

These experiments induced us to subject also the β-dichloromuconic acid to the action of reducing agents with the view of determining whether the one or the other hydromuconic acid be formed. The reduction was brought about by sodium amalgam, and by tin and hydrochloric acid, the latter agent being found to be most convenient for the preparation of hydromuconic acid from α-dichloromuconic acid (*cf.* the following paper). Like Bode's acid, so also is the β-acid readily attacked by tin and hydrochloric acid. On adding the acid to the hot reducing mixture, it dissolves, and the solution poured off from the tin, on cooling, deposits crystals, which when recrystallised from water melt at 195°. These gave on analysis numbers corresponding with the formula $C_6H_8O_4$:—

	Theory.	Found.
C	50·0	49·87
H	5·55	5·52

Tin and hydrochloric acid reduce, therefore, the β-acid to the same hydromuconic acid as that obtained from Bode's dichloromuconic acid.

The reduction of β-dichloromuconic acid by sodium amalgam was carried out in the cold, and according to the directions given by v. Baeyer and Rupe (*loc. cit.*) for the α-acid. The product formed melted at 195°, that is, the acid was identical with the hydromuconic acid obtained in using the acid reducing agent.

Further experiments are necessary to establish the constitution of β-dichloromuconic acid and its relation to Bode's acid.

In describing the separation of the β-acid, it was mentioned that the various ethereal extracts, though frequently taken up with water, still yielded some of the ordinary sparingly soluble dichloromuconic acid. This leads to the conclusion that another acid is formed by the action of phosphorus pentachloride on mucic acid, which on boiling with water gradually undergoes a transformation into Bode's acid. In fact, when the product of the action after removal of the α-dichloromuconic acid is shaken with ether, the solvent evaporated, and the substance left behind taken up with water, the cold, clear solution on heating deposits the characteristic needles of Bode's acid. This is only sparingly soluble in hydrochloric acid, and the dichloromuconic acid which Bode got from the filtrate is undoubtedly formed during the evaporation of the neutralised liquid.

It may also be further mentioned that the α- and β-dichloromuconic acids are not the immediate products of the action of phosphorus pentachloride on mucic acid, but that these acids are, as might be expected, the result of a decomposition of the first formed tetrachloradipic acid. The isolation of this acid has been undertaken by one of us (S. R.) and S. F. Dufton. The result of our experiments we hope, in a short time, to bring before the Society.

University Laboratory,
Cambridge.

LXII.—*Contributions to the Knowledge of Mucic Acid.* Part III. *Hydromuconic Acid.*

By S. Ruhemann, Ph.D., M.A.

The view with regard to the constitution of the unsaturated acid, isomuconic acid, which I published together with F. F. Blackman, (*Trans.*, 1890, 370), was based on the assumption that the hydromuconic acid melting at 195° has the formula

$$COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH,$$

which had been first suggested by v. Baeyer (*Berichte*, **18**, 680). The recent researches of v. Baeyer and Rupe (*Annalen*, **256**, 1) have changed this view. They proved that the reduction-product of Bode's dichloromuconic acid has the constitution

$$COOH{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CH_2{\cdot}COOH,$$

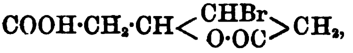
and that this acid, when boiled with sodium hydroxide, suffers transformation to $\Delta^{\alpha\beta}$-hydromuconic acid,

$$COOH{\cdot}CH{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}COOH.$$

Their interesting paper deals further with the action of potash on dibromadipic acid, $COOH\cdot CH_2\cdot CHBr\cdot CHBr\cdot CH_2\cdot COOH$, which results in the formation of an acid called by them *muconic acid*. This compound which we had studied at the same time, and described as isomuconic acid, has, according to their researches, the formula $COOH\cdot CH{:}CH\cdot CH{:}CH\cdot COOH$.

The hydromuconic acid which formed the starting point of our experiments was prepared by reducing Bode's dichloromuconic acid with tin and hydrochloric acid. I have, since then, used this method and found it more convenient than the reduction by sodium amalgam, at least in the preparation of larger quantities of hydromuconic acid. The reduction takes place very readily. It is only necessary to add the dichloromuconic acid to the hot reducing mixture, to pour off from the tin as soon as the organic acid is dissolved, to cool the solution, to collect the hydromuconic acid crystallised out, and to concentrate the filtrate. One recrystallisation is sufficient for the purification of the acid. The hydromuconic acid which remains together with the stannous chloride in the last mother liquor was not extracted, but the quantity can only be small. In an operation in which the dichloromuconic acid prepared from 450 grams of mucic acid was reduced by tin and hydrochloric acid, the hydromuconic acid obtained amounted to 65 grams; while, if one takes into consideration that only under most favourable circumstances, 25 per cent. of the mucic acid is transformed into dichloromuconic acid, the abovementioned quantity of mucic acid can theoretically yield no more than 76 grams.

In repeating the action of bromine on a hot aqueous solution of hydromuconic acid, it was found that the crystals which separated out first were dibromadipic acid, identical with that formed by adding bromine to hydromuconic acid dissolved in glacial acetic acid, and that the needles which crystallised out a few hours afterwards were a monobromhydromuconic acid. The latter was not pure but contained traces of dibromadipic acid, as was indicated by the analysis and by the formation of a small quantity of muconic acid (as I call the isomuconic acid according to v. Baeyer and Rupe's proposal) on boiling with potash and then acidifying. These observations were, as mentioned before (*loc. cit.*), different from those of Marquardt (*Annalen*, **165**, 253). v. Baeyer and Rupe, in the paper referred to, have also repeated this reaction, and found that the dibromadipic acid thus formed is identical with that produced on acting with bromine on a glacial acetic acid solution of hydromuconic acid; whilst, on the other hand, they confirmed Marquardt's statement as to the bromhydromuconic acid. These contradictory results can only be explained as follows:—

In the action of bromine on $\Delta^{\beta\gamma}$-hydromuconic acid dissolved in water, there may be formed, besides dibromadipic acid, according to the conditions, either Marquardt's monobromhydromuconic acid, or that which we observed. As both the acids last mentioned are undoubtedly the result of a splitting off of hydrobromic acid from the dibromadipic acid first formed, and as Marquardt's acid would have, according to v. Baeyer and Rupe's researches, the constitution $COOH{\cdot}CH{:}CH{\cdot}CHBr{\cdot}CH_2{\cdot}COOH$, the formation of the other monobromo-acid may be explained by the removal of the γ-bromine-atom, and the hydrogen of the carboxyl-group. The formula of this acid may thus be expressed by  $COOH{\cdot}CH_2{\cdot}CH{<}{}^{CHBr}_{O{\cdot}OC}{>}CH_2$, that is, this acid may be regarded as the lactone of bromoxyadipic acid.

As the bromine-derivative was found to be very unstable, and could not be recrystallised without suffering decomposition, I studied the action of chlorine on hydromuconic acid.

Dichloradipic Acid.—On saturating a solution of hydromuconic acid in glacial acetic acid with chlorine, no crystals separated. The solution, when evaporated, leaves a crystalline residue which on recrystallisation from water, yields colourless needles, melting at 210° with decomposition. They are readily soluble in alcohol and in boiling water, and gave on analysis values corresponding to the formula $COOH{\cdot}CH_2{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2{\cdot}COOH$:—

	Theory for $C_6H_8Cl_2O_4$.	Found. I.	Found. II.
C	33·49	33·50	—
H	3·72	3·9	—
Cl	33·02	—	33·12

The ethereal salt of dichloradipic acid was prepared in the usual manner by saturating an alcoholic solution of the acid with hydrogen chloride, allowing it to stand for some hours, pouring the liquid into water, and extracting with ether. On evaporating the solvent, an oil was left which solidified to colourless plates melting at 48—49°.

Analysis proved this substance to be the *ethyl salt of dichloradipic acid.* The formula $COOC_2H_5{\cdot}CH_2{\cdot}CHCl{\cdot}CHCl{\cdot}CH_2{\cdot}COOC_2H_5$ requires:—

	Theory for $C_{10}H_{16}Cl_2O_4$	Found.
C................	44·28	44·26
H	5·9	5·91

The constitution of dichloradipic acid is analogous to that of the dibromo-acid; this follows from the fact that the ethereal salt, as well as the acid, when heated with alcoholic potash yields the potassium salt of muconic acid, from which mineral acids set free the acid, as proved by its properties, and by an analysis which gave:—

	Theory for $C_6H_6O_4$.	Found.
C	50·70	50·84
H	4·22	4·31

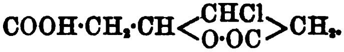
The action of chlorine on an aqueous solution of hydromuconic acid leads to dichloradipic acid, and to a monochlorhydromuconic acid; the reaction, therefore, takes place in exactly the same manner as with bromine.

A hot aqueous solution of hydromuconic acid was saturated with chlorine; the liquid, which on cooling did not deposit crystals, was allowed to stand for a few days over sulphuric acid in a vacuum, when a small quantity of needles separated, which, by their melting point and the change to muconic acid they suffer under the influence of potash, were identified as dichloradipic acid.

The filtrate from these crystals when concentrated at a low temperature yielded, on cooling, long needles which melted at 119—120°, dissolved readily in water and in alcohol, and gave on analysis numbers corresponding with the formula $C_6H_7ClO_4$:—

	Theory.	Found.	
		I.	II.
C	40·33	40·81	—
H	3·92	4·16	—
Cl	19·89	—	19·92

This compound has, therefore, the composition of a monobromhydromuconic acid. Its behaviour leads to the view that it may be regarded as the lactone of chloroxyadipic acid,

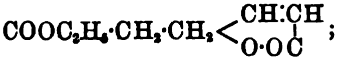


$$COOH\cdot CH_2\cdot CH<\begin{matrix}CHCl\\ O\cdot OC\end{matrix}>CH_2.$$

Experiments were made with the object of proving this formula by preparing the ethyl salt and determining whether only one ethyl-group enters into the acid. The chlorinated acid is readily etherified, but on attempting to distil it, hydrogen chloride was given off, and at 180—182° under a pressure of 20 mm., an oil passed over which did not contain more than 5·19 per cent. of chlorine. On adding strong aqueous ammonia to this oil, muconamide is formed, as was proved by its properties, and by a nitrogen determination, which gave:—

	Calculated for $C_6H_8N_2O_2$.	Found.
N	20·0	20·18

formation of muconamide from the chlorinated acid is explained, if the constitution suggested above is assumed latter. The ethereal salt of this acid, on distillation, loses en chloride, and is partially transformed into the ethyl salt lactone of hydroxyhydromuconic acid,



$$COOC_2H_5\cdot CH_2\cdot CH_2<\begin{matrix}CH{:}CH\\ O\cdot O\overset{|}{C}\end{matrix};$$

ia removes hydrogen chloride completely, and produces first nide of hydroxyhydromuconic acid,

$$CONH_2\cdot CH_2\cdot CH(OH)\cdot CH{:}CH\cdot CONH_2,$$

iowever, loses water and yields muconamide,

$$CONH_2\cdot CH{:}CH\cdot CH{:}CH\cdot CONH_2.$$

interesting is the action of boiling water on the chlorinated this behaviour agrees well with the lactonic nature of this he acid cannot be treated with water without suffering deion; hydrogen chloride is constantly given off, and on evapoie solution the long, characteristic needles disappear, and nt crystals of a different habit crystallise out, which are free rine. This transformation is brought about more readily by ie aqueous solution of the chlorinated acid in a flask furnished flux condenser. The crystals which separate out on concennerally melted at about 100—105°, but on recrystallising, ig point was raised, until it had reached 122—125°, when no iange was observed. In spite of the differences in the oints, the various specimens had all the same composition; be regarded as stereochemical isomerides.

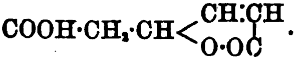
no doubt that this substance is identical with the product npricht (*Annalen*, 165, 253) got by the action of silver ibromadipic acid. He observed also the changing of the ints and found that this does not alter the composition.

to prove the composition of this acid, I have analysed the lting at 122—125°; Limpricht used the low-melting acid s.

	Theory for $C_6H_6O_4$.	Found.
C	50·7	50·56
H	4·22	4·35

determined the basicity of the acid with the same speciund in accordance with Limpricht that it is monobasic. alising 0·2355 gram of the acid with titrated potash solution, a volume was used containing 0·0927 gram KHO; this corresponds to 39·18 per cent.; the calculated percentage being 39·43.

Limpricht called this acid muconic acid; v. Baeyer and Rupe, however, have adopted this name for the previously described (*loc. cit.*) substance, while they express the view that the former compound may be regarded as the lactone of hydroxyhydromuconic acid,



$$COOH{\cdot}CH_2{\cdot}CH<\begin{matrix}CH{:}CH\\ O{\cdot}OC\end{matrix}.$$

This suggestion is supported by the experiments which I have described above.

The crystallographic measurements of this acid have been kindly undertaken by Mr. R. H. Solly, Demonstrator at the Mineralogical Laboratory of this University.

Crystals melting at 122—125°.

Oblique.

101, 100 = 66° 13½′; 111, 010 = 33° 55′; 101, 001 = 55° 20½′.
β, 58° 26′

$a : b : c = 1{\cdot}80811 : 1 : 1{\cdot}62515.$

Forms observed:—*a*100; *c*001; *n*011; *f*111; *s*$\bar{1}$11.

Angles calculated.		Angles found.		
ac =	121° 34′	121° 22′	121° 34′*	121° 44′
af =	77	77*	77° 4	77 11
fn =	30 51	30 27	30 31	30 37
fs =	54 11½	53 30	53 55	54 50
cf =	71 30	71 19	71 30*	71 58
fm =	34 21	*m*110 not observed.		
$ms_{\mid}$ =	27 3			
$s_{\mid}c$ =	47 6			
cn =	54 9½			
$ff_{\mid}$ =	67 50	67° 42½′	67° 53′	68° 12′

A great number of crystals were measured, and the extreme angles are given; those marked with an * were the best angles, and were taken to calculate the elements—the faces *n* and *s* gave poor reflections, but their position was accurately determined by zones.

The crystals are limpid and give fairly good reflections. The development of the faces varies a good deal; sometimes the crystals consist of a number of parallel growths on the *f* faces, other times *f*, *c*, and *a* equally developed with small *s* and *n*, Fig. 1. *Cleavage a*, highly perfect.

FIG. 1.

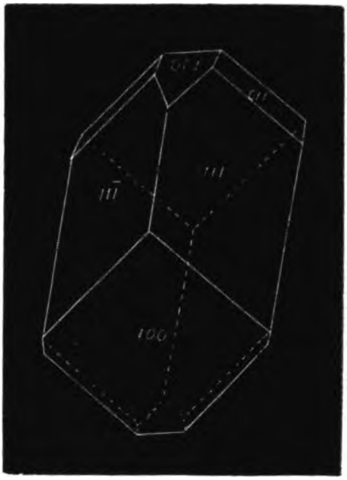


FIG. 2.

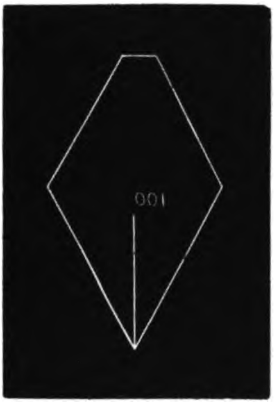
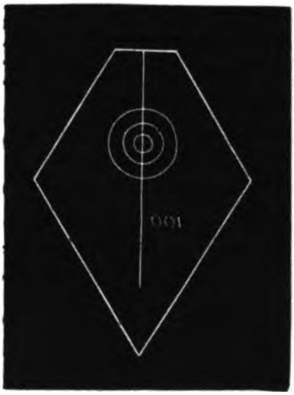


FIG. 3.



Optical Characters.—The cleavage plane *a* is very nearly perpendicular to an optic axis and gives an optic picture in convergent polarised light, resembling cane-sugar, Fig. 2. Double refraction negative. The arrangement of colours about the eye was symmetrical to the plane of symmetry, and the mean lines were seen to lie in this plane.

Crystals melting at 100—105°.

These crystals resemble the last in habit and development, but an accurate crystallographic determination was impossible on account of the dull and rounded development of the faces. The forms usually present were *a*, *f*, and *c*, the angle between *a* and *f* was found to be 85° 50′, and ff_1, 55—57°.

Cleavage a, highly perfect.

Optical Characters.—A cleavage plate gave a distinctly different optic picture to the last crystals, as is shown in Fig. 3; instead of one eye nearly in the centre of the field, only a curved hyperbolic arm with a small eye is seen at the extreme edge of the field.

Double refraction, negative.

University Laboratory,
Cambridge.

LXIII.—*Diphenylfurfuran.*

By W. H. **Perkin**, Jun., Ph.D., F.R.S., and **Aug. Schloesser**, Ph.D., M.Sc.

The constitution of carbuvic acid (carbopyrotritartaric acid) and uvic acid (pyrotritartaric acid) has, since the discovery of these acids by Harrow (Trans., 1878, 425), been the subject of most careful investigation.

Harrow first obtained these acids by boiling ethyl diacetylsuccinate, $\begin{array}{l}CH_3{\cdot}CO{\cdot}CH{\cdot}COOEt\\ CH_3{\cdot}CO{\cdot}CH{\cdot}COOEt\end{array}$, with dilute sulphuric acid:—

$$C_{12}H_{18}O_6 + H_2O = \underset{\text{Carbuvic acid.}}{C_8H_8O_5} + 2C_2H_5{\cdot}OH.$$

$$C_8H_8O_5 = \underset{\text{Uvic acid.}}{C_7H_8O_3} + CO_2.$$

Knorr (*Ber.*, **17**, 2866) subsequently obtained the ethereal salt of carbuvic acid directly from ethyl diacetylsuccinate by the action of concentrated sulphuric acid:—

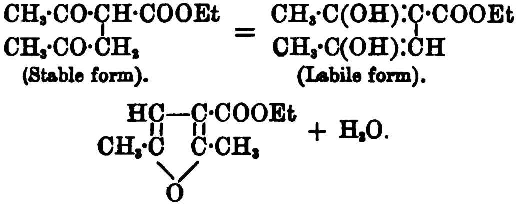
$$\begin{array}{l}CH_3{\cdot}CO{\cdot}CH{\cdot}COOEt\\ CH_3{\cdot}CO{\cdot}CH{\cdot}COOEt\end{array} = C_8H_6O_5Et_2 + H_2O.$$

Paal (*Ber.*, **17**, 2765) showed that ethyl acetonylacetoacetate, when warmed with concentrated hydrochloric acid, yielded ethyl uvate, thus:—

$$\begin{array}{l}CH_3{\cdot}CO{\cdot}CH{\cdot}COOEt\\ CH_3{\cdot}CO{\cdot}CH_2\end{array} = C_7H_7O_3Et + H_2O.$$

uing from these and other facts, Knorr and Paal concluded that ric and uvic acids are furfuran-derivatives, the former being the e latter the mono-carboxylic acid of dimethylfurfuran.

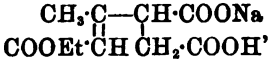
formation of ethyl uvate, for example, from ethyl acetonyl-cetate would be represented by the equation

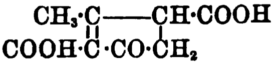


(Stable form). (Labile form).

Ethyl uvate (dimethylfurfurancarboxylate).

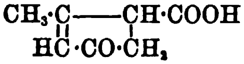
: acid was subsequently obtained by Fittig (*Ber.*, 18, 3410, 34), from methronic acid, by the elimination of carbon dioxide. nic acid is formed by the condensation of ethyl acetoacetate dium succinate in the presence of acetic anhydride.

g (*Annalen*, 250, 71) is of the opinion that in this reaction a salt,  $\begin{array}{l}CH_3\cdot C—CH\cdot COONa\\ COOEt\cdot CH\;CH_2\cdot COOH\end{array}$, is first formed, and this then mol. H_2O, forming the sodium ethyl salt of methronic acid. nic and uvic acids would therefore have the following e:—



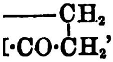
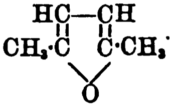
$$\begin{array}{l}CH_3\cdot C\text{——}CH\cdot COOH\\ COOH\cdot C\cdot CO\cdot CH_2\end{array},$$

Methronic acid.

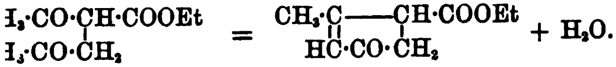


$$\begin{array}{l}CH_3\cdot C\text{——}CH\cdot COOH\\ HC\cdot CO\cdot CH_2\end{array}.$$

Uvic acid.

ill be seen at a glance that Fittig's formula for uvic acid very materially from that proposed by Paal and Knorr; the supposes this acid to be a derivative of a closed carbon chain,  $\begin{array}{l}\text{——}CH_2\\ [\cdot CO\cdot CH_2\end{array}$, whereas according to the latter, this acid is a derivative of dimethylfurfuran, .

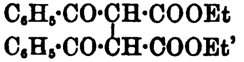
: explains Knorr's synthesis of ethyl carbuvate from ethyl succinate and Paal's synthesis of ethyl uvate from ethyl acetoacetate on the assumption that in both cases a simple oxide condensation takes place, thus:—



$$\begin{array}{l}I_3\cdot CO\cdot CH\cdot COOEt\\ I_3\cdot CO\cdot CH_2\end{array} = \begin{array}{l}CH_3\cdot C\text{——}CH\cdot COOEt\\ HC\cdot CO\cdot CH_2\end{array} + H_2O.$$

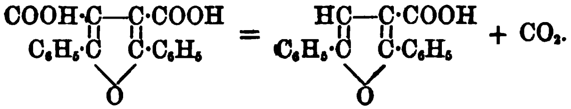
yl acetonylacetoacetate. Ethyl uvate.

The general behaviour of these substances towards reagents, and particularly the fact that they do not combine with phenylhydrazine or hydroxylamine, favours very strongly the view that they are furfuran-derivatives; but, on the other hand, it is difficult, as Fittig points out, to explain the formation of dimethylfurfuran-derivatives by the condensation of succinic acid with ethyl acetoacetate.

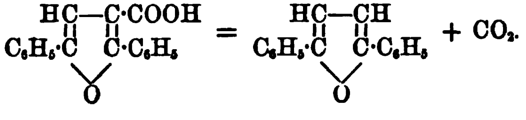
In a paper published some time since (Trans., 1885, **47**, 271; compare also Trans., 1886, **49**, 166—171), it was shown, by one of us, that ethyl dibenzoylsuccinate,  $\begin{array}{l}C_6H_5\cdot CO\cdot CH\cdot COOEt \\ C_6H_5\cdot CO\cdot CH\cdot COOEt\end{array}$, when dissolved in concentrated sulphuric acid, underwent condensation, giving rise to an ethereal salt, $C_{22}H_{20}O_5$, which in its reactions showed great similarity to ethyl carbuvate. On hydrolysis, it was converted into a bibasic acid (diphenylfurfurandicarboxylic] acid),* $C_{18}H_{12}O_5$, which corresponded to carbuvic acid; from which, however, it appeared to differ in that when heated it yielded an anhydride, whereas carbuvic acid, under similar treatment, is decomposed into uvic acid and carbonic anhydride.

At that time, owing to the difficulty in obtaining material, these experiments were left unfinished; in view, however, of the importance of assigning the correct formulæ to these derivatives, we have again taken up the subject and now beg to lay the results of our experiments before the Society.

The action of heat on diphenylfurfurandicarboxylic acid has now been carefully investigated, and our experiments have shown that this acid when rapidly and strongly heated is readily decomposed with evolution of carbon dioxide and formation of diphenylfurfuranmonocarboxylic acid—



This acid is again readily decomposed into carbon dioxide and diphenylfurfuran, thus:—



Diphenylfurfuranmonocarboxylic acid has already been prepared by

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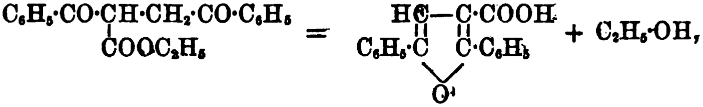
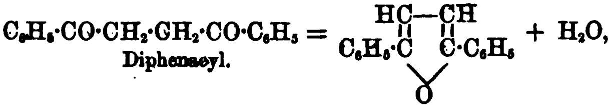
* In this paper, these acids are considered as furfuran-derivatives for the sake of simplicity.

Kapf and Paal (*Ber.*, **21**, 1489 and 3054) by acting on ethyl phenacylbenzoylacetate with hydrochloric acid,



and possesses the same melting point (217°) and the same properties as the acid obtained from diphenylfurfurandicarboxylic acid.*

Paal also prepared diphenylfurfuran by heating phenylacetylene-benzoylacetic acid, $\underset{\text{COOH}}{C_6H_5{\cdot}CO{\cdot}CH{\cdot}C{:}C{\cdot}C_6H_5}$, or diphenacyl, with fuming hydrochloric acid at 130—150°,

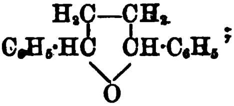


this substance being also identical with the diphenylfurfuran obtained by us.*

If diphenylfurfuran is submitted to the vapour of bromine, it is converted into a beautifully crystalline compound, $C_{16}H_{10}Br_4O$, which melts at 191°,

$$C_{16}H_{12}O + 3Br_2 = C_{16}H_{10}Br_4O + 2HBr,$$

and when treated with sodium and alcohol, diphenylfurfuran is readily reduced with formation of a variety of products depending on the amount of sodium employed. In studying this reaction, Paal (*Ber.*, **21**, 3057) obtained diphenyltetrahydrofurfuran,



but we found, on repeating this experiment, that if a large excess of sodium is employed, diphenylfurfuran takes up as many as eight atoms of hydrogen, forming octohydrodiphenylfuran, $C_{16}H_{20}O$, the two phenyl-groups being apparently partially reduced.

In preparing considerable quantities of diphenylfurfuran, a small quantity of a secondary product was obtained, which crystallised in yellow needles and on analysis gave numbers agreeing with the formula $C_{34}H_{20}O_2$. This substance is obviously formed by the condensation of two molecules of diphenylfurfuranmonocarboxylic acid, the reaction being similar to the formation of anthraquinone from benzoic acid,

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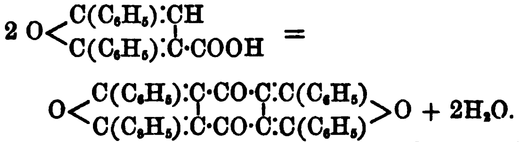
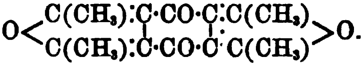
* Through the kindness of Dr. Paal, I have been enabled to institute a direct comparison of his and my derivatives, and have found them to be identical in every respect.



$$2\,O<\begin{matrix}C(C_6H_5):CH\\ C(C_6H_5):C\cdot COOH\end{matrix} = O<\begin{matrix}C(C_6H_5):C\cdot CO\cdot C:C(C_6H_5)\\ C(C_6H_5):C\cdot CO\cdot C:C(C_6H_5)\end{matrix}>O + 2H_2O.$$

Carbuvic acid.

In studying the action of heat on carbuvic acid, Paal (*Ber.*, **20**, 1086) isolated a substance, tetramethyluvinone,[*] which corresponds in every respect with the condensation-product just described; to this he gave the formula



$$O<\begin{matrix}C(CH_3):C\cdot CO\cdot C:C(CH_3)\\ C(CH_3):C\cdot CO\cdot C\,C(CH_3)\end{matrix}>O.$$

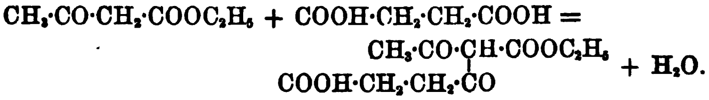
We propose to name our product tetraphenyluvinone.

In studying these results, it is obvious that whatever the constitution of carbuvic acid may be, the substances described above can only be furfuran-derivatives, because in the formation of these substances from ethylic dibenzoylsuccinate, owing to the absence of methyl-groups no mesityl oxide condensation, such as that suggested by Fittig, can take place.

As, however, the internal condensation of ethyl diacetylsuccinate runs so exactly parallel with that of ethyl dibenzoylsuccinate, and as in both cases products so exactly similar in properties are produced, it is extremely probable that carbuvic acid and diphenylfurfurandicarboxylic acid are similarly constituted.

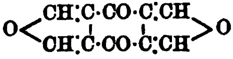
Supposing methronic acid to be a furfuran-derivative, its formation from ethyl acetoacetate and succinic acid by Fittig's synthesis might be explained thus:—

I. In the first place, condensation takes place between the methylene-group of the ethyl acetoacetate and one carboxyl-group of the succinic acid, thus:—

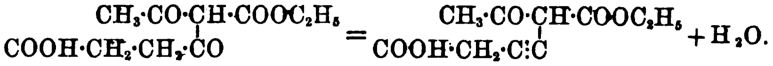


$$CH_3\cdot CO\cdot CH_2\cdot COOC_2H_5 + COOH\cdot CH_2\cdot CH_2\cdot COOH = \begin{matrix}CH_3\cdot CO\cdot CH\cdot COOC_2H_5\\ COOH\cdot CH_2\cdot CH_2\cdot CO\end{matrix} + H_2O.$$

---

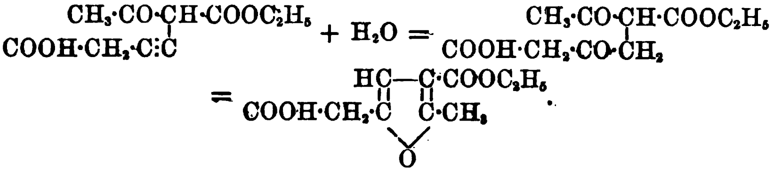
[*] This substance was originally termed uvinone by Dr. Paal, but I have recently received a communication from him in which he agrees with me that the term uvinone is best applied to the parent-substance  $O<\begin{matrix}CH:C\cdot CO\cdot C:CH\\ CH:C\cdot CO\cdot C:CH\end{matrix}>O$ and that consequently his compound should be termed tetramethyluvinone.

II. This intermediate product, under the influence of the dehydrating agents employed, loses 1 mol. H_2O, thus:—

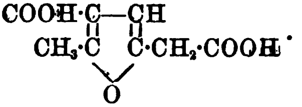


$$\begin{array}{r}CH_3\cdot CO\cdot CH\cdot COOC_2H_5\\ COOH\cdot CH_2\cdot CH_2\cdot CO\end{array} = \begin{array}{r}CH_3\cdot CO\cdot CH\cdot COOC_2H_5\\ COOH\cdot CH_2\cdot C{:}C\end{array} + H_2O.$$

III. A substance of this constitution is, as Paal has repeatedly shown, readily converted into a furfuran-derivative, thus:—



According to this explanation, methronic acid would be represented by the formula

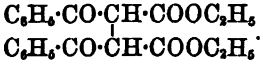


This formula fully explains the isomerism of methronic and carbuvic acids, and also the fact that the former acid, on heating, is converted into uvic acid and carbon dioxide. Should the above prove to be the correct explanation of the formation of methronic acid and other acids obtained by similar reactions by Fittig, this will be an interesting example of the transference of an oxygen-atom from one carbon-atom to the neighbouring carbon-atom, thus:—

$$\begin{array}{c}\cdot CH_2\cdot CO\cdot\\ \text{or}\\ \cdot CH{:}C(OH)\cdot\end{array} = \cdot C{:}C\cdot + H_2O = \begin{array}{c}\cdot CO\cdot CH_2\cdot\\ \text{or}\\ \cdot C(OH){:}CH\cdot\end{array}.$$

This simultaneous splitting off and reverse addition of the elements of water was first suggested by Baeyer (*Ber.*, **3**, 70).

Ethyl Dibenzoylsuccinate,



$$\begin{array}{l}C_6H_5\cdot CO\cdot CH\cdot COOC_2H_5\\ C_6H_5\cdot CO\cdot CH\cdot COOC_2H_5\end{array}.$$

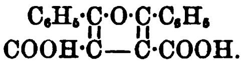
This ethereal salt was first prepared by the action of iodine on the dry sodium compound of ethyl benzoylacetate suspended in ether (Trans., 1885, **47**, 263).

As it was necessary in this research to prepare considerable quantities of this substance, numerous experiments were first made with the view of finding the conditions which gave the best yield. As the result of these the following method was ultimately adopted.

2·5 grams of sodium, in the form of very fine wire, was placed in a flask containing 500 c.c. of absolute ether, and 20 grams of ethyl benzoylacetate was then added in small portions at a time, the contents of the flask being carefully cooled during the operation by a stream of cold water. The sodium compound of ethyl benzoylacetate soon separated out, and the mass ultimately became quite thick. The action is allowed to go on for about three hours, the contents of the flask being violently agitated from time to time, in order to prevent the particles of sodium from being covered with the white sodium compound and thus rendered inactive. 14 grams of iodine, dissolved in absolute ether, was now allowed to run in slowly from a dropping funnel, the flask being well agitated during the operation. The resulting slightly brownish solution was mixed with water, the slight excess of iodine removed by the addition of a few drops of sulphurous acid, the ethereal layer separated, washed once with water, dried over calcium chloride, and the ether distilled off. The slightly yellowish oily residue, on standing, almost completely solidified to a mass of crystals of crude ethyl dibenzoylsuccinate. This crude product is best purified by trituration in a mortar with cold methylated spirit, in which the crystals are very sparingly soluble, separation of the dark-coloured mother liquor by filtration, and recrystallisation of the almost colourless residue from boiling purified methylated spirit.

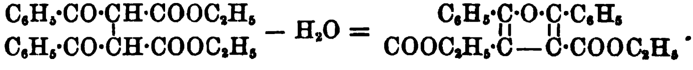
100 grams of ethyl benzoylacetate by this process yielded from 65 to 70 grams of pure ethyl dibenzoylsuccinate.

Diphenylfurfurandicarboxylic Acid,



$$\begin{array}{c} C_6H_5{\cdot}C{\cdot}O{\cdot}C{\cdot}C_6H_5 \\ \| \qquad \| \\ COOH{\cdot}C{-}C{\cdot}COOH. \end{array}$$

Solution in sulphuric acid converts ethyl dibenzoylsuccinate quantitatively into ethyl furfurandicarboxylate, thus :—

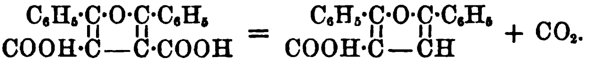


$$\begin{array}{c} C_6H_5{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \\ | \\ C_6H_5{\cdot}CO{\cdot}CH{\cdot}COOC_2H_5 \end{array} - H_2O = \begin{array}{c} C_6H_5{\cdot}C{\cdot}O{\cdot}C{\cdot}C_6H_5 \\ \| \qquad \| \\ COOC_2H_5{\cdot}C{-}C{\cdot}COOC_2H_5 \end{array}.$$

The details of this operation have already been given (Trans., 1886, **49**, 166). In a number of cases it was noticed that the solution of ethyl dibenzoylsuccinate in concentrated sulphuric acid acquired in the first place a deep brownish colour, which on standing for 12 hours gradually became green, and, lastly, of an intense indigo-blue.

The pure ethereal salt was hydrolysed by boiling on a water-bath, for about 15 minutes, with twice the calculated quantity of alcoholic potash. On mixing the ethereal salt with alcoholic potash, the very sparingly soluble potassium salt of the bibasic acid separates out almost immediately (compare carbopyrotritartaric acid), in glittering needles. These are brought into solution by the addition of water, the excess of alcohol removed by evaporation, and the bibasic acid precipitated by the addition of an acid. The precipitate is collected, washed with water, and purified by recrystallisation from methylated spirit.

Diphenylfurfurandicarboxylic acid melts at 238°, and when strongly heated splits up into diphenylfurfuranmonocarboxylic acid and carbon dioxide, thus :—



$$\begin{array}{c}C_6H_5{\cdot}C{\cdot}O{\cdot}C{\cdot}C_6H_5\\ \|\qquad\| \\ COOH{\cdot}C{-}C{\cdot}COOH\end{array} = \begin{array}{c}C_6H_5{\cdot}C{\cdot}O{\cdot}C{\cdot}C_6H_5\\ \|\qquad\|\\ COOH{\cdot}C{-}CH\end{array} + CO_2.$$

The 1 : 2 position of the carboxyl-groups in diphenylfurfurandicarboxylic acid is clearly proved by the ease with which this acid is converted into its anhydride. This interesting compound has already been prepared in small quantities (Trans., 1885, **47**, 268); but in view of its importance in discussing the formula of diphenylfurfurandicarboxylic acid, we have again prepared and analysed this substance.

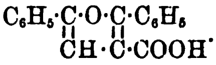
A beautiful specimen of the anhydride, twice recrystallised from acetic anhydride, gave the following results on analysis :—

0·1357 gram substance gave 0·3691 gram CO_2 and 0·0428 gram H_2O.

	Theory for $C_{18}H_{10}O_4$.	Found.
C	74·48 per cent.	74·17 per cent.
H	3·45 „	3·50 „
O	22·07 „	22·33 „

The properties of this anhydride have already been given (*loc. cit.*, p. 269).

Diphenylfurfuranmonocarboxylic Acid,



$$\begin{array}{c}C_6H_5{\cdot}C{\cdot}O{\cdot}C{\cdot}C_6H_5\\ \|\qquad\|\\ CH{\cdot}C{\cdot}COOH\end{array}.$$

In preparing this acid, pure diphenylfurfurandicarboxylic acid is heated in a round-bottomed flask, by a bath of fusible metal, until it melts, and the temperature is then gradually raised until a rapid evolution of carbon dioxide takes place. After heating for about five minutes, the effervescence slackens considerably, when the mass is poured into hot dilute sodium hydrate solution, heated nearly to boiling, in order to prevent the sparingly soluble sodium salt of the monocarboxylic acid from separating, and filtered through a hot water funnel. A considerable quantity of a dark-brownish substance remains on the filter paper; this consists of crude diphenylfurfuran. and will be referred to later on. On acidifying the dark-coloured solution of the sodium salt, a white, crystalline substance is precipitated, which consists for the most part of diphenylfurfuranmonocarboxylic acid, mixed with varying quantities of unchanged bibasic acid. This was collected, washed with water, dried on a porous plate in a water-oven, and repeatedly extracted with small quantities of boiling benzene, in which the bibasic acid is very sparingly soluble. The solution on standing deposited the new acid in slender, white needles, which, after repeated recrystallisation from benzene, were readily obtained pure. The analysis gave the following numbers:—

0·1727 gram substance gave 0·4901 gram CO_2 and 0·0736 gram H_2O.

	Theory. $C_{17}H_{12}O_3$.	Found.
C	77·27 per cent.	77·42 per cent.
H	4·54 „	4·73 „
O	18·18 „	18·85 „

Diphenylfurfuranmonocarboxylic acid melts at about 214—217°. It is almost insoluble in water and light petroleum, readily soluble in boiling alcohol, acetic acid, and benzene.

The basicity of this acid was determined by titration with a standard solution of potassium hydrate.

0·6470 gram of acid required for neutralisation 24·8 c.c. of potassium hydrate solution, 1 c.c. of which contained 0·002786 gram KOH.

The amount of KOH used was therefore 0·06909 gram, whereas theory requires for a monobasic acid $C_{17}H_{12}O_3$, 0·06861 gram. The *silver salt* was prepared by dissolving the acid in a slight excess of dilute ammonia, allowing the solution to stand over sulphuric acid till neutral, and then precipitating with silver nitrate. It is a white, insoluble powder, which is only very slowly affected by light. The analysis of the salt dried at 100° gave the following numbers:—

0·2042 gram substance gave 0·0602 gram Ag.

	Theory. $C_{17}H_{11}O_3Ag$.	Found.
Ag	29·11 per cent.	29·48 per cent.

Experiments were next instituted with the object of demonstrating the absence of a hydroxyl- or carbonyl-group in diphenylfurfurancarboxylic acid.

a. 2 grams of the pure acid was boiled for three to four hours with an excess of acetic anhydride on a reflux apparatus. The acid soon dissolved, but no other change was noticed. After distilling off the greater bulk of the anhydride, water was added, and the whole allowed to stand. The white, crystalline precipitate melted at 215°, and was found to be unaltered diphenylfurfuranmonocarboxylic acid.

b. 0·5 gram of pure acid was dissolved in an excess of potassium hydrate solution, 0·2 gram of hydroxylamine hydrochloride, dissolved in a little water, added, and the product allowed to stand for 48 hours. The solution was then acidified with dilute hydrochloric acid, the precipitate collected, washed, and dried at 100°. Its melting point was found to be 215—217°, and it was therefore unchanged acid.

Diphenylfurfurancarboxylic acid, as described above, is identical with $\alpha\alpha'$-diphenylfurfuran-β-carboxylic acid obtained by Paal (*Ber.*, **21**, 1489) by boiling phenylacetylenebenzoylacetic acid with alcohol and fuming hydrochloric acid. In addition to the properties given above, Paal noticed that the acid on oxidation gives a quantitative yield of benzoic acid. An account of the salts of this acid, including the ethyl salt ($C_{19}H_{16}O_3$, m. p. 82°), is also given.

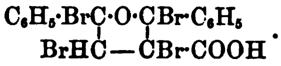
Action of Bromine on Diphenylfurfurancarboxylic Acid.

The finely divided acid was exposed under a bell-jar to the fumes of bromine. The acid first appeared to melt, but after some hours it again completely solidified. The residual darkly-coloured mass was placed over soda-lime to remove excess of bromine, and thus obtained as a pinkish, extremely insoluble powder, which could not be obtained in a crystalline condition. It was repeatedly extracted with small quantities of hot alcohol, and the resulting colourless powder analysed, with the following result:—

0·1536 gram substance gave 0·1993 gram AgBr.

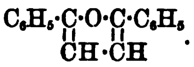
	Theory. $C_{17}H_{12}O_3Br_4$.	Found.
Br	54·98 per cent.	55·34 per cent.

Judging from the results obtained in our experiments on the action of bromine on diphenylfurfuran, it is extremely probable that the brominated acid has the constitution—



$$\begin{array}{l} C_6H_5\cdot Br\overset{}{C}\cdot O\cdot CBr\cdot C_6H_5 \\ \quad\;\; | \qquad\; | \\ \quad BrHC-CBr\cdot COOH \end{array}.$$

Diphenylfurfuran,



$$\begin{array}{c} C_6H_5\cdot C\cdot O\cdot C\cdot C_6H_5 \\ \| \qquad \| \\ CH\cdot CH \end{array}.$$

This substance is formed, together with diphenylfurfuranmonocarboxylic acid, by the action of heat on diphenylfurfurandicarboxylic acid. On treating the product of the reaction with dilute sodium hydrate (see above), diphenylfurfuran is left behind as a brownish, crystalline mass. This was washed well with water, dried on a porous plate in a desiccator, and repeatedly extracted with boiling light petroleum (b. p. 70—90). By this means diphenylfurfuran is dissolved, leaving a varying quantity of a very sparingly soluble yellow substance, which will be described below.

The dark-coloured solution is evaporated, the residue transferred to a small retort, and very rapidly distilled under reduced pressure (50 mm.). The yellowish distillate is dissolved in a little boiling light petroleum, from which solvent, on cooling, pure diphenylfurfuran separates in colourless, glittering, fern-like crystals.

The analysis gave the following results:—

0·1592 gram substance gave 0·5086 gram CO_2 and 0·0787 gram H_2O.

	Theory. $C_{16}H_{12}O$.	Found.
C	87·27 per cent.	87·13 per cent.
H	5·46 ,,	5·49 ,,
O	7·27 ,,	7·38 ,,

Diphenylfurfuran melts at 88—89°, and has all the properties ascribed to this substance by Paal, who, however, gives the melting point as 91°.

Tetrabromodiphenylfurfuran, $C_{16}H_{10}Br_4O$.

In order to study the action of bromine on diphenylfurfuran, the finely divided substance was spread out on a sheet of glass, and exposed under a bell-jar to the vapours of bromine for 24 hours. On opening the bell-jar, it was noticed that considerable quantities of hydrogen bromide had been produced. The dark-coloured residue was placed over soda-lime till free from excess of bromine, and then once or twice recrystallised from benzene.

In this way beautiful, thin, colourless, satiny needles were obtained, which on analysis gave the following numbers:—

I. 0·1948 gram substance gave 0·0326 gram H_2O and 0·2580 gram CO_2.
II. 0·1834 gram substance gave 0·0302 gram H_2O and 0·2380 gram CO_2.
III. 0·2078 gram substance gave 0·2922 gram AgBr.
IV. 0·2190 gram ,, 0·3061 gram AgBr.

	Theory. $C_{16}H_{10}Br_4O$.	Found. I.	II.	III.	IV.	
C	35·69 p. c.	36·12	35·39	—	—	p. c.
H	1·85 „	1·86	1·82	—	—	„
Br	59·48 „	—	—	59·81	59·47	„

Tetrabromodiphenylfurfuran melts at 190—191°. It is readily soluble in boiling benzene, carbon bisulphide, and acetic acid; sparingly soluble in hot alcohol and light petroleum. When quickly heated, in small quantities, it sublimes apparently unchanged. The substance is indeed characterised by its extreme stability; even boiling with zinc-dust and acetic acid seems to have little influence on it.

Reduction of Diphenylfurfuran.

In his experiments on diphenylfurfuran, Paal (*Ber.*, **21**, 3057) found that when this substance is reduced in alcoholic solution by sodium it is converted into tetrahydrodiphenylfurfuran, $C_{16}H_{16}O$ (a colourless oil boiling at 320—322°).

We have carried out a number of experiments on this same subject, and find that in this reaction a variety of products are formed, according to the amount of sodium used. Thus, if slightly more than the theoretical quantity for 4 atoms of hydrogen is employed, an oil is obtained which has properties very similar to those assigned by Paal to tetrahydrodiphenylfurfuran; this on analysis gives numbers agreeing fairly well with this formula:—

0·1530 gram substance gave 0·1061 gram H_2O and 4802 gram CO_2.

	Theory. $C_{16}H_{16}O$.	Found.
C	85·71 per cent.	85·53 per cent.
H	7·14 „	7·69 „

If, on the other hand, a large excess of sodium is employed, diphenylfurfuran takes up 8 atoms of hydrogen, and is converted into octohydrodiphenylfurfuran. The details of the preparation of this substance are the following.

Pure diphenylfurfuran (10 grams) is dissolved in boiling absolute alcohol (300 grams), and a large excess of sodium (25—30 grams) added as quickly as possible, a little more alcohol being added from time to time if necessary. The product is mixed with water, the alcohol boiled off, and the residue extracted two or three times with ether. The ethereal solution is washed with water, dried over calcium chloride, the ether distilled off, and the residual, almost colourless oil purified by repeated fractionation under diminished pressure.

Two preparations were made and analysed.

I. The oil boiled at 210—220°, under a pressure of 40 mm.

0·1570 gram substance gave 0·1236 gram H_2O and 0·4842 gram CO_2.

II. The oil boiled at 245—250°, under a pressure of 110 mm.

0·1596 gram substance gave 0·4940 gram CO_2 and 0·1276 gram H_2O.

	Theory.	Found.	
	$C_{16}H_{20}O$.	I.	II.
C	84·21 per cent.	84·11	84·41 per cent.
H	8·77 „	8·75	8·84 „

Tetraphenyluvinone, $C_{34}H_{20}O_4$.

This substance is produced in small quantity in the preparation of diphenylfurfuran, and, being very insoluble, remains behind after extracting the crude product with light petroleum or benzene, as described above. The crude yellow residue is readily purified by recrystallisation from boiling xylene.

Analysis:—

0·1513 gram substance gave 0·0575 gram H_2O and 0·4590 gram CO_2.

	Theory. $C_{34}H_{20}O_4$.	Found.
C	82·93 per cent.	82·74 per cent.
H........	4·07 „	4·22 „
O	13·00 „	13·04 „

Tetraphenyluvinone crystallises from xylene, in which it is only sparingly soluble, in thin, brilliant, yellow needles, which are often grouped together in tufts. It does not melt at 280°. It is very sparingly soluble in boiling alcohol, benzene, acetic acid, and most other organic solvents. On exposure to light, the crystals rapidly become of a deep orange colour.

Prolonged boiling with zinc-dust and acetic acid dissolves the substance, forming a reddish solution from which water precipitates a salmon-coloured, amorphous precipitate. Fusion with potash causes the substance to char.

The following property is highly characteristic of tetraphenyluvinone. If the smallest trace of the substance be added to concentrated sulphuric acid, a most intense dark-green solution is produced, which possesses a most magnificent dark, brick-red fluorescence. If the solution be strongly heated, the green colour gradually changes to a pure blue without influencing the fluorescence. A drop of nitric acid added to the sulphuric acid solution produces a red coloration out fluorescence. The colour and fluorescence of the sulphuric solution instantly disappear on adding water.

rperiments on the absorption spectrum and general optical pro- es of the solution are in progress.

eriot Watt College, Edinburgh.

LXIV.—*Note on the Reduction of Aromatic Amides.*

A. HUTCHINSON, B.A., Scholar of Christ's College, Cambridge.

he year 1874, Guareschi (*Ber.*, 7, 1462) observed that by the n of sodium amalgam in acid solution benzamide is reduced to yl alcohol. Emil Fischer has recently pointed out that the les of the fatty series do not exhibit this reaction, and as differ- s of this kind between aromatic and aliphatic compounds offer y points of interest, I have, at Professor Fischer's request, tried ction of sodium amalgam on numerous other amides, and venture to lay before the Society a brief sketch of the results so far ined.

y experiments show that the amides of those aromatic acids in h the carboxyl-group is directly joined to the benzene-nucleus eadily attacked by 2½ per cent. sodium amalgam in acid solution, corresponding alcohol being generally produced in fair quantity. orthotoluylamide yielded about 38 per cent. of orthotolyl ol, the rest of the amide being converted into a resin, and to the nt of from 7—10 per cent. into a white, crystalline substance, h contained nitrogen and melted between 154° and 155°. licylamide gave 42 per cent. saligenin and a brown resin, whilst parahydroxybenzamide considerable quantities of parahydroxy- yl alcohol were obtained.

some cases, from anisamide for example, analogues of benzil hydrobenzoïn have also been obtained. I have found, on the hand, that the amides of those aromatic acids in which the oxyl-group is situated in a side chain cannot be reduced by m amalgam; thus all attempts to reduce phenylacetamide have entirely futile, while the amide of cinnamic acid gives phenyl- ionamide only.

rther experiments are now in progress, and I hope shortly to ish a detailed account of the whole research.

emical Laboratory, University of Würzburg.

LXV.—*Some Improved Vacuum Joints and Taps.*

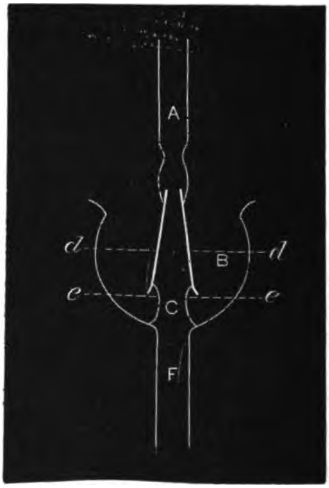
By W. A. **Shenstone**, Lecturer on Chemistry in Clifton College.

The apparatus described in this paper has already been found to be helpful, and as it seems likely to be of use to chemists and physicists, I venture to offer a description of it to the Chemical Society. The idea of such a joint as the improved cup joint shown by Fig. 1 occurred to me some years ago in connection with some experiments upon which I was then engaged jointly with Mr. J. Tudor Cundall. I found, on mentioning the matter to my colleague, that a similar idea had occurred to him also, and, indeed, that he had already commenced the construction of what I will suggest should be called a *Cundall cup joint*. The rest of the apparatus described in this note has been devised by me recently for my own use, or for the use of others.

The Cundall Cup Joint.

It often happens, after two or more pieces of apparatus have been connected by means of a liquid joint of the ordinary pattern, that it becomes necessary to part them again. In doing this, more or less of the liquid by which the joint is sealed is almost inevitably admitted to the interior of the apparatus, where its presence may be very objectionable. The new joint prevents this entirely, and it can be made by any moderately good worker in glass. It is so simple in construction that the diagram (Fig. 1) almost explains itself. A

Fig. 1.



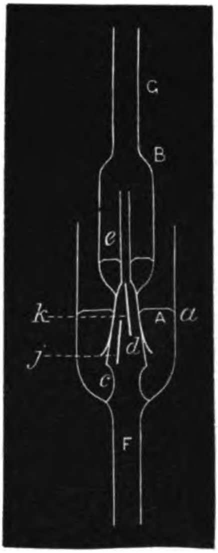
tube, F, carries a cup, B, into which it projects at C, the end C being slightly tapered and ground to fit another tube, A, which passes over it. When the joint has been sealed, by introducing any suitable liquid into B up to the level *dd*, the joint can be broken and remade without any of the liquid entering F. It is best, however, to empty B to the level *ee*, and to cleanse the ground joint before its parts are reunited.

Joints capable of Withstanding Pressure from within as well as from without.

Attention has lately been called to the need of joints able to resist pressure from within by Mr. J. T. Bottomley, F.R.S., in a paper "On a Constant-volume Air-thermometer" (*Phil. Mag.*, **26**, 149); and I believe that those described below will be found to be satisfactory. They are quite easy to construct, and can be made of any glass, including hard glass, by a fairly good glass worker.

A tube, F, carries a cup, A, and a narrow projecting tube, *de*. The latter is expanded and tapered at *d*, as shown in the diagram (Fig. 2). An outer tube, B, is ground to fit the projecting tube *de* at A. B is expanded just above its mouth, and contracted to any convenient size at G. Two small grooves, *j*, *k*, are cut into the ground surfaces of the

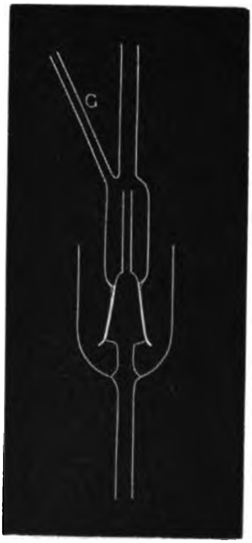
Fig. 2.



joint, one on the projecting tube, the other on B, of such length that when they are brought into one straight line they overlap and give free communication between the inside of B and the cup A; but so that when they are not in one straight line no liquid can pass from A to B, or *vice versâ*. To make the joint, B is fitted to A, mercury or any other suitable liquid is placed in the cup A, and *k* and *j* are brought into one straight line; the liquid in A can then be readily sucked into B, so that it stands at the levels *a* and *e*. A or B is then slightly turned, and the joint is complete. If circumstances do not permit of the liquid being drawn into B by reduction of pressure, the cup A may be made somewhat deeper, in order that, by filling A above the level *e*, mercury may be forced into B by its own pressure.

Fig. 3 shows a modification of this joint, in which the liquid, employed to seal the joint against internal pressure, can be introduced by means of a side tube, G, which is afterwards closed before the blowpipe. This form of joint is useful when the two parts may not be rotated.

FIG. 3.

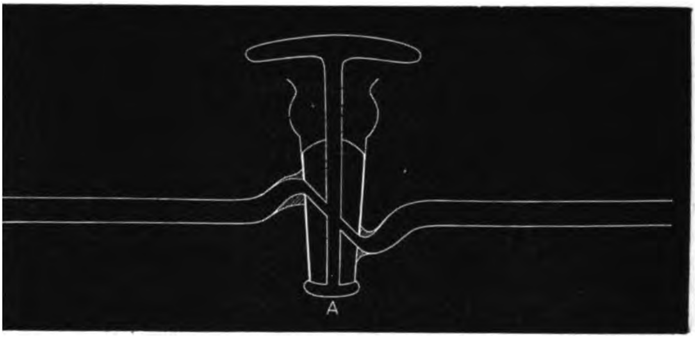


These joints, as will be seen, enable one, with the help of flexible spiral glass tubes, to attach movable manometers to other apparatus with a degree of security against leakage such as has hitherto only been attainable by the use of joints sealed before the blowpipe, which, h not very difficult to make, are often inconvenient when a series perimenta has to be made.

A True Vacuum Tap.

the safety or vacuum taps previously described, so far as I am inted with them, are open to the very serious objection that they ikely to retain more or less air in the space A (Fig. 4) under-h the plug of the tap, and that this air will gradually leak into apparatus with which the tap is employed. Experience shows it is not safe to avoid this by filling A with mercury or any r liquid, but I have overcome the difficulty by drilling the plug he tap as shown in Fig. 4, so that the space at A is in free com-ication with the rest of the apparatus.

Fig. 4.



s will be seen, this improvement can easily be applied to taps ady in stock, or even in use, with very little risk or expense.

LXVI.—*The Production of Camphor from Turpentine.*

By J. E. Marsh, B.A., and R. Stockdale, B.A.

formation of camphor from turpentine has been accomplished several chemists, but, probably owing to the smallness of the d, the camphor so obtained has never been very fully examined, has its relationship to natural camphor, on the one hand, and urpentine on the other, been satisfactorily ascertained.

n this preliminary note we describe two methods by which camphor can be obtained from turpentine in fairly large quantity; and at the same time we give some account of the various products obtained, which are of interest in tracing the connection between turpentine, camphene, and camphor.

Both processes depend, in the first instance, on the production of the solid hydrochloride of turpentine, the so-called "artificial camphor."

In the first process employed, this hydrochloride is distilled over moderately hot soda-lime, to obtain camphene; then, after a partial purification, the camphene is shaken up with a strong solution of hydrochloric acid to convert it into camphene hydrochloride. This is heated with acetate of potassium and glacial acetic acid to give acetate of borneol; and finally, the acetate of borneol, when saponified with alcoholic potash, yields *borneol*.

The second process employed is simple, and seems to give a more satisfactory yield. The terpene hydrochloride is heated with potassium acetate and glacial acetic acid in sealed tubes at about 250°, when it gives a high-boiling liquid which, on saponification, yields *borneol*.

The turpentine employed was the ordinary dextrorotatory australene. It was allowed to stand for some time over dry carbonate of potash, and then distilled, when it boiled fairly constantly at 158—159°, the temperature being allowed to rise to 163° at the end. Its sp. gr. was found to be—

$$0{\cdot}8705 \text{ at } \frac{9{\cdot}5^\circ \text{ turpentine}}{15{\cdot}5^\circ \text{ water}}.$$

Its rotatory power (determined with a Laurent half-shade polarimeter) was found to be—

$$[\alpha]_D = +11{\cdot}3^\circ \text{ at } 9{\cdot}5^\circ.$$

The hydrochloride was prepared by saturating the turpentine with gaseous hydrogen chloride, and crystallising from alcohol the solid product obtained.

The rotatory power of the hydrochloride was determined in alcoholic solution—

$$[\alpha]_D = +4{\cdot}8^\circ.^*$$

---

* We are unable to confirm the observation of Wallach and Conrady (*Annalen*, 252, 156) or of Pesci (Abstr., 1889, 158), that dextropinene chlorhydrate is inactive. We have made several determinations, and always found the substance to be dextrorotatory, but it is not the optical isomer of the chlorhydrate of French turpentine. The names + and − pinene are therefore hardly suitable for these terpenes.

Production of Camphene.

Several methods for obtaining camphene from terpene hydrochloride were tried, for example, distilling with soap, and heating with alcoholic potash. The most satisfactory method for obtaining the substance quickly, and in large quantity, was found to be the distillation of the hydrochloride over moderately heated granular soda-lime. The camphene so obtained boils at about 160°, and is a liquid, being kept in solution evidently by small quantities of liquid impurity. Indication was, however, obtained that the camphene could be separated in the solid form, either by freezing or by partial oxidation with chromic mixture. But these processes were not adopted, as being unnecessary for our purpose.

Preparation of Borneol.

The camphene was then shaken up with fuming hydrochloric acid, and the solid substance which separated was collected on a filter, pressed, and dried. This was heated with potassium acetate and glacial acetic acid at about 200° for three hours. On then separating and distilling, it gave some camphene and a considerable quantity of a higher-boiling liquid, presumably the acetate of borneol, which was not specially purified, but at once saponified with alcoholic potash.

The product of saponification, when distilled, yielded a solid of high melting point and camphorous odour. A portion was still further purified, by sublimation, for analysis. It melted at about 200°, and gave :—

	Found.	Calculated for $C_{10}H_{18}O$.
C........	78·04 per cent.	77·92 per cent.
H........	12·16 „	11·68 „

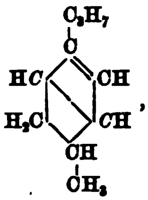
The substance is, therefore, borneol.

Borneol direct from Terpene Hydrochloride.

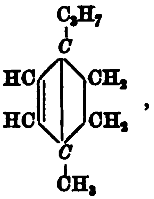
The second method for obtaining borneol is much less tedious than the one just described in that it is not necessary to first prepare camphene. Wallach (*Annalen*, **239**, 6) has given a method for preparing camphene by heating terpene hydrochloride, 1 part, sodium acetate, 1 part, and glacial acetic acid, 2 parts, for 3—4 hours, at a temperature approaching 200°. A slight modification of this process yields acetate of borneol, as well as, and apparently in larger quantity than, camphene.

The mixture was heated in sealed tubes for 3—4 hours at about 250°, each tube containing 20 grams of terpene hydrochloride, 12 of potassium acetate, and 10 c.c. of glacial acetic acid. When cold, the contents of the tubes were distilled in steam, the distillate separated from water, dried, and distilled. From the lower-boiling portion camphene was readily obtained in the solid state (b. p. 154—156°), whilst a considerable portion distilled above 190°, condensing as a liquid. This was saponified with alcoholic potash, when borneol was obtained. This crude borneol was oxidised by nitric acid, when an inactive camphoric acid was obtained.

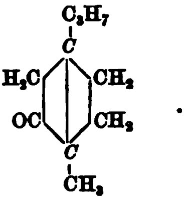
Professor Wallach, in his masterly investigation of the terpenes, has given some consideration to the constitution of turpentine, which he calls pinene, of camphene, and of camphor. He represents their constitution by the following formulæ:—



Pinene.



Camphene.



Camphor.

Such formulæ as these, whatever their justification, are certainly open to criticism, both on general and on particular grounds. In the first place, are the compounds which they represent to be regarded as hexamethylene- or as double tetramethylene-derivatives? In the latter case, why should hexagonal symbols be retained? In the former case, have we any evidence of cross-linking between carbon-atoms in the 1 : 4-position? And if we adduce anthracene as an instance, ought not pinene to resemble anthracene, and be capable of yielding a quinone on oxidation? Consider further the remarkable rearrangement of nuclei in passing from pinene to camphene, as expressed by the symbols. Have we any analogy for such a change? It is, for example, as if quinoline, by a simple reaction, could yield isoquinoline, or as if a homonucleal substituted naphthalene could yield a heteronucleal, and *vice versâ*. Then, again, the more obvious characters of camphoric acid are inconsistent with Wallach's camphor formula.

But, perhaps, the strongest argument against these formulæ is derived from the application to them of the hypothesis of the asymmetric carbon-atom. Professor Wallach accepts, in general, that the rotatory power of a body is conditioned by the presence of an asymmetric carbon-atom, but he is scarcely consistent in following out the consequences of the theory. One of these consequences is, that any exchange of groups or linkages about an asymmetric carbon-atom must lead to the production of an inactive body, as far as concerns the rotatory power due to that carbon-atom. For since there is an equal chance for the formation of both optically opposite isomers, they will both be found in equal quantity.

On the other hand, simple substitution, or the alteration of groups by oxidation, &c., will not necessarily affect the optical isomerism.

Camphor then and camphoric acid obtained from an active pinene, which has been found to yield an active camphene, should be themselves active. We find, however, that camphoric acid obtained from active pinene is inactive. Moreover, if camphene and camphor are to be regarded, according to Wallach's formulæ, simply as unsaturated hexamethylene-derivatives, then they are in no case capable of rotatory power, for the formulæ do not possess a non-superposable image.

Without in any way presuming to detract from the high merit of Professor Wallach's experimental work, we venture to submit that his formulæ for pinene, camphene, and camphor are inconsistent with the properties and reactions of those compounds, and without analogy in organic chemistry.

University Laboratory, Oxford.

LXVII.—*p-Desylphenol.*

By Francis R. Japp, F.R.S., and G. H. Wadsworth, Associate of the Normal School of Science.

100 grams of benzoïn and 150 grams of phenol were melted together, cooled, and gradually poured, while still liquid, into 1500 grams of concentrated sulphuric acid, stirring all the time. The temperature rose, and the solution assumed a dark reddish-brown colour. After standing over night, the mixture was poured, in a thin stream, into four times its bulk of cold water. A white substance, which proved to be a sulphonic acid, separated; part of this went into solution in the warm liquid, but was deposited on cooling, and the whole precipitate was thus obtained in a crystalline form, in which it could be readily filtered off.

In the first experiments which we made, the sulphuric acid was carefully cooled during the addition of the benzoïn and phenol, and the mixture was afterwards poured upon pounded ice. This procedure, however, offers no advantages over the foregoing.

The white sulphonic acid was separated by filtration, freeing it as far as possible from adhering sulphuric acid by means of the filter-pump, but not washing it, as it is far more soluble in pure water than in dilute sulphuric acid. It was then made into a thick cream with strong hydrochloric acid, and heated in sealed tubes at 150° during from three to four hours. The hydrolysed compound separated as a dark-coloured, amorphous mass in the tubes. It was boiled with a solution of sodium carbonate, in which it first fused and afterwards solidified; then it was washed with water, dried, and dissolved in hot benzene. From this solution it was deposited, on long standing, in thick, crystalline crusts consisting of hard, warty aggregations of needles, containing benzene of crystallisation (*vide infra*). It was recrystallised twice from benzene, and finally, for analysis, from light petroleum, from which it separates in minute, colourless laminæ melting constantly at 133°. It crystallises from dilute alcohol in large, very thin plates. It is readily soluble in caustic alkalis, and is precipitated from the solution by carbon dioxide, showing that it contains a phenolic hydroxyl-group. Under a pressure of 45 mm., it boils without decomposition at 309—314°.

Analysis agreed with the formula $C_{20}H_{16}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·2342	0·7149	0·1142
II	0·1939	0·5905	0·0987

	Calculated for $C_{20}H_{16}O_2$.		Found.	
			I.	II.
C_{20}	240	83·33	83·24	83·04
H_{16}.......	16	5·56	5·41	5·65
O_2	32	11·11	—	—
	288	100·00		

Dr. Klingemann had the kindness to determine the molecular weight of the compound by Raoult's method, using acetic acid as a solvent:—

				Mol. wt.	
Wt. subst.	Wt. solv.	$\frac{\text{Wt. subst.} \times 100}{\text{Wt. solv.}}$.	Depression.	Found.	Calc. for $C_{20}H_{16}O_2$.
0·3525	19·943	1·768	0·22°	313	288

(Molecular depression of acetic acid = 39.)

The crystals deposited from benzene have the formula $C_{20}H_{16}O_2,C_6H_6$.

It is difficult to air-dry them without efflorescence; hence only 20 per cent. of benzene was found, instead of the calculated 21·3 per cent.

In order to ascertain the composition of the sulphonic acid which is first formed, the calcium salt was prepared and analysed. For this purpose, the sulphonic acid, after filtering it from the dilute sulphuric acid as already described, was dissolved in hot sodium carbonate, from which solution a sparingly soluble sodium salt separated on cooling; this was purified by recrystallisation from boiling alcohol, which deposited it in tufts of lustrous, yellowish, flat needles or laminæ. In order to convert it into the calcium salt, it was dissolved in hot water, and the solution precpitated with calcium chloride. The calcium salt was washed with cold water, air-dried, and analysed. It is a crystalline, yellow powder, which dissolves sparingly in boiling water, and is re-deposited on cooling.

0·3870 gram, on heating at 140°, lost 0·0554 gram H_2O, and the resulting 0·3316 gram anhydrous salt, on ignition with sulphuric acid, gave 0·0582 gram $CaSO_4$.

	Calculated for $(C_{20}H_{15}O_2{\cdot}SO_3)_2Ca,7H_2O$.	Found.
H_2O in 100 parts	14·00	14·31

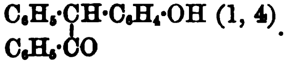
	Calculated for $(C_{20}H_{15}O_2{\cdot}SO_3)_2Ca$.	Found.
Ca in 100 parts	5·16	5·15

The compound $C_{20}H_{16}O_2$ is formed from benzoïn and phenol according to the equation

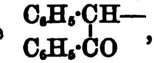
$$C_{14}H_{12}O_2 + C_6H_5{\cdot}OH = C_{20}H_{16}O_2 + H_2O,$$

the product being further converted into a sulphonic acid in the process.

A study of the reactions of the compound $C_{20}H_{16}O_2$ has led us to assign to it the constitution



$$\begin{array}{l}C_6H_5{\cdot}CH{\cdot}C_6H_4{\cdot}OH\ (1,4)\\ C_6H_5{\cdot}CO\end{array}.$$

Adopting the convenient name "desyl" which Victor Meyer has proposed for the radicle  $\begin{array}{l}C_6H_5{\cdot}CH—\\ C_6H_5{\cdot}CO\end{array}$, such a compound might be termed *p-desylphenol*.

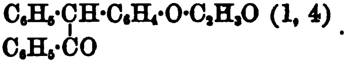
The elimination of water occurs between the hydroxyl-group of the benzoïn and the para-hydrogen-atom of the phenol, and the condensation thus resembles those of fatty alcohols with phenol described by Liebmann (*Ber.*, **14**, 1842), in which, however, zinc chloride was used as a dehydrating agent. We, therefore, tried to condense benzoïn and phenol with zinc chloride, so as to avoid the formation of the sulphonic acid, but without success.

Action of Acetic Anhydride.—*p*-Desylphenol was heated in a sealed tube with acetic anhydride for three hours at 150°; the excess of the anhydride was distilled off on the water-bath under reduced pressure, and the last traces destroyed by evaporation with alcohol. The product was twice recrystallised from light petroleum (b. p. 90—120°), from which it was deposited in slender, white needles melting at 106—107°. From alcohol, it crystallises in well-developed, oblique prisms. Under a pressure of about 40 mm., it distils without decomposition between 325° and 330°. Analysis showed that a monacetyl-derivative had been formed:—

	Substance.	CO_2.	H_2O.
I	0·2008	0·5894	0·0991
II	0·1540	0·4504	0·0765

	Calculated for $C_{22}H_{18}O_3$.		Found.	
			I.	II.
C_{22}.........	264	80·00	80·04	79·76
H_{18}	18	5·45	5·48	5·52
O_3	48	14·55	—	—
	330	100·00		

Acetyl-p-desylphenol has the formula



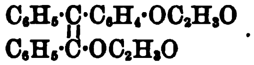
$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}H\cdot C_6H_4\cdot O\cdot C_2H_3O\ (1, 4) \\ C_6H_5\cdot CO \end{array}$$

By heating *p*-desylphenol with acetic anhydride for three hours at 200°, a *diacetyl*-derivative is obtained. The compound was purified by recrystallisation from benzene, from which it is deposited in hemispherical aggregates of small, colourless needles melting constantly at 186—187°.

	Substance.	CO_2.	H_2O.
I........	0·2043	0·5793	0·1024
II........	0·2048	0·5811	0·1047

	Calculated for $C_{24}H_{20}O_4$.		Found.	
			I.	II.
C_{24}	288	77·41	77·33	77·38
H_{20}	20	5·37	5·56	5·68
O_4	64	17·22	—	—
	372	100·00		

ɔ formation of a diacetyl-derivative can be accounted for on the ıption that at the high temperature of the reaction the group O of the *p*-desylphenol passes into the tautomeric tertiary form)H), which is then acetylated. The compound would thus have ɪrmula



$$\begin{array}{l} C_6H_5\cdot C\cdot C_6H_4\cdot OC_2H_3O \\ \quad\| \\ C_6H_5\cdot C\cdot OC_2H_3O \end{array}$$

th the monacetyl- and the diacetyl-derivative, when boiled with ic potash, regenerate *p*-desylphenol.

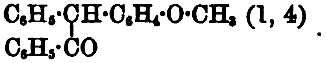
)esylanisoïl.—In methylating *p*-desylphenol, we employed a od introduced by Japp and Klingemann (Trans., 1888, 526) in ıethylation of pyruvaldehydrazone. This method, which ensures ıete alkylation, has since been used with good results by Victor ɪr, Beckmann, and others.

ıe desylphenol was dissolved in methyl alcohol with 4 molecular ɔrtions of methyl iodide, and into this mixture, which was kept ıg in a flask fitted with a reflux condenser, a solution of four .ic proportions of sodium in methyl alcohol was gradually ɪed to drop, so that the operation lasted about four hours. The ter part of the alcohol was then distilled off, caustic soda was d, so as to keep in solution any unchanged substance, if present, the new compound was precipitated with water. The filtered line solution gave no turbidity with hydrochloric acid, showing the alkylation had been complete. The substance was distilled ɪr reduced pressure, passing over between 292° and 298° under ım. pressure. It was finally recrystallised three times from light ɔleum, and formed colourless aggregates of flat needles melting)—92°. It is insoluble in caustic alkalis, showing that the methyl replaced hydrogen of the phenolic hydroxyl. Analysis led to the ıula $C_{21}H_{18}O_2$:—

	Substance.	CO_2.	H_2O.
I.	0·2141	0·6538	0·1158
II.	0·2181	0·6663	0·1174

	Calculated for $C_{21}H_{18}O_2$.		Found.	
			I.	II.
C_{21}	252	83·44	83·28	83·32
H_{18}	18	5·96	6·00	5·98
O_2	32	10·60	—	—
	302	100·00		

The compound is, therefore, *p-desylanisoïl*,



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}H\cdot C_6H_4\cdot O\cdot CH_3\ (1,4) \\ C_6H_5\cdot CO \end{array}$$

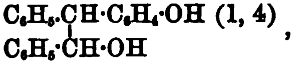
The foregoing method of alkylation was adopted in view of the possibility that the hydrogen-atom of the CH-group might also be replaced by methyl. That no such reaction occurred is in keeping with the observation made by Victor Meyer and Oelkers (*Ber.*, **21**, 1300) that only one hydrogen-atom of the methylene-group in deoxybenzoïn can be replaced by alkyl. In the present case, this first hydrogen-atom is already replaced by the group $—C_6H_4\cdot O\cdot CH_3$; the second does not react.

Reduction with Sodium and Amyl Alcohol.—10 grams of *p*-desylphenol were dissolved in excess of amyl alcohol, and 6·5 grams of metallic sodium were gradually added to the boiling liquid. The amyl alcoholic solution was shaken with dilute hydrochloric acid, washed with water, and distilled down to a small bulk, finally removing the remainder of the amyl alcohol on the water-bath under reduced pressure. The product was recrystallised from benzene, which deposited it in tufts of slender, colourless needles melting constantly at 161—162°. It is soluble in caustic alkalis. Analysis led to the formula $C_{20}H_{18}O_2$:—

	Substance.	CO_2.	H_2O.
I	0·2025	0·6133	0·1124
II	0·2220	0·6725	0·1256

	Calculated for $C_{20}H_{18}O_2$.		Found.	
			I.	II.
C_{20}	240	82·75	82·59	82·61
H_{18}.	18	6·20	6·16	6·28
O_2	32	11·05	—	—
	290	100·00		

The compound has the constitution



$$\begin{array}{l} C_6H_5\cdot \underset{|}{C}H\cdot C_6H_4\cdot OH\ (1,4) \\ C_6H_5\cdot CH\cdot OH \end{array},$$

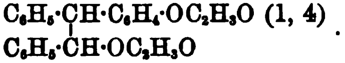
and may be termed *hydrodesylphenol*.

When it is heated with excess of acetic anhydride for three hours at 150°, it yields a diacetyl-derivative. This compound was purified by recrystallisation from a mixture of benzene and light petroleum. It forms groups of needles melting at 156—157°. Analysis gave figures agreeing with the formula $C_{24}H_{22}O_4$:—

	Substance.	CO_2.	H_2O.
I	0·2045	0·5767	0·1080
II	0·2008	0·5659	0·1027

	Calculated for $C_{24}H_{22}O_4$.		Found.	
			I.	II.
C_{24}	288	77·00	76·91	76·85
H_{22}	22	5·88	5·85	5·68
O_4	64	17·12	—	—
	374	100·00		

It has the constitution

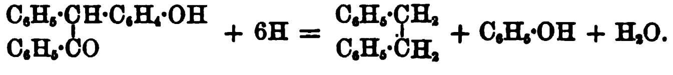


$$\begin{array}{l} C_6H_5\cdot CH\cdot C_6H_4\cdot OC_2H_3O \ (1, 4) \\ C_6H_5\cdot CH\cdot OC_2H_3O \end{array}$$

Reduction with Hydriodic Acid.—*p*-Desylphenol was heated with fuming hydriodic acid and amorphous phosphorus for four hours at 130°, after which the contents of the tube were poured into water, extracted with ether, and the ethereal solution decolorised with sulphurous acid. The ethereal solution was shaken with caustic soda, to remove any phenolic compound. On acidifying this alkaline solution and distilling with steam, ordinary phenol passed over, which was identified by the precipitate with bromine-water, and the violet coloration with ferric chloride.

On evaporating the ethereal solution, thus freed from phenol, an oil was left, which smelt like dibenzyl, and, after distillation under reduced pressure, solidified. The crystalline mass was dissolved in alcohol, but as nothing separated over night, a minute crystal of dibenzyl was added, when the substance was at once deposited in large laminæ, which, after recrystallisation from alcohol, melted at 52—53° (m. p. of dibenzyl 51·5—52·5°), and gave on analysis figures agreeing with those required for dibenzyl. Calculated for $C_{14}H_{14}$: C 92·30, H 7·69. Found: C 92·10, H 7·80 per cent.

The reduction with hydriodic acid, therefore, takes place according to the equation



$$\begin{array}{l} C_6H_5\cdot CH\cdot C_6H_4\cdot OH \\ C_6H_5\cdot CO \end{array} + 6H = \begin{array}{l} C_6H_5\cdot CH_2 \\ C_6H_5\cdot CH_2 \end{array} + C_6H_5\cdot OH + H_2O.$$

The ease with which this reaction, which, according to this equation, involves a separation of carbon from carbon, occurs at the relatively low temperature of 130° led us at first to doubt whether the desyl-group really was attached to the nucleus of the phenol. The result of the fusion with potash, however, decides this question in the affirmative.

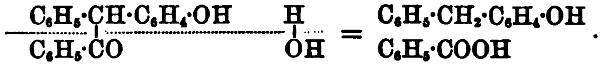
Fusion with Caustic Potash.—*p*-Desylphenol was fused with 10 parts of caustic potash mixed with 1 part of water, and kept at a temperature of 200—210°. At first the fused potassium salt of *p*-desylphenol floated as a yellow liquid on the surface of the potash; but by continually stirring it, it was converted into a pulverulent, grey salt, which was disseminated throughout the mass. At this point the reaction is complete. The melt was dissolved in water, nearly neutralised with hydrochloric acid, and carbon dioxide passed in to precipitate phenols. After separating the precipitate by filtration, hydrochloric acid was added to the filtrate, which was then extracted with ether. On distilling off the ether, a large quantity of benzoic acid was obtained.

The precipitate formed with carbon dioxide was recrystallised from alcohol, and afterwards from a mixture of benzene and petroleum, from which it was deposited in groups of large, flat, obliquely truncated needles melting constantly at 84—85°. Analysis agreed with the formula $C_{13}H_{12}O$.

0·2010 gram gave 0·6252 CO_2 and 0·1178 H_2O.

	Calculated for $C_{13}H_{12}O$.		Found.
C_{13}	156	84·78	84·83
H_{12}	12	6·52	6·51
O	16	8·70	—
	184	100·00	

The compound is identical with *p*-benzylphenol, the melting point of which is given at 84° (Paternò, Rennie). Its formation from *p*-desylphenol may be expressed as follows:—



$$\frac{C_6H_5{\cdot}CH{\cdot}C_6H_4{\cdot}OH}{C_6H_5{\cdot}CO} \quad \frac{H}{OH} = \frac{C_6H_5{\cdot}CH_2{\cdot}C_6H_4{\cdot}OH}{C_6H_5{\cdot}COOH}.$$

This reaction proves conclusively that the desyl-group is attached to the nucleus of the phenol, and it may also be taken as showing, so far as the evidence afforded by a potash fusion can be admitted, that desylphenol is a para-derivative.

The decomposition of *p*-desylphenol into benzylphenol and benzoic acid appears also to take place slowly with strong aqueous caustic potash at 100°.

If a higher temperature is employed in the foregoing fusion, the *p*-benzylphenol is in turn broken up, and a mixture of *p*-hydroxybenzoic acid and benzoic acid is obtained. The *p*-hydroxybenzoic acid, after separating it from the benzoic acid, was identified by its melting point, and by the reaction with bromine-water. The yield was good, so that the acid could not have been formed by the oxidaf benzoic acid, as in Barth's experiment on the fusion of benzoic vith caustic potash (*Annalen*, **164**, 141).

the foregoing reactions are in harmony with the constitution of ımpound as *p*-desylphenol.

have failed, however, to obtain direct proof of the presence of a ic carbonyl-group, as the substance does not react either with lhydrazine or with hydroxylamine, although it was treated with reagents under a variety of the most favourable conditions.

ıight be concluded from this that the compound does not contain ›onyl-group, and exists only in the tertiary or hydroxylic form it exhibits in its diacetyl-derivative. The high temperature, er, required for the introduction of the second acetyl-group against this view. The inability to react with phenylhydrazine ʼdroxylamine is rather, we think, to be explained by the observa- V. Meyer and Oelkers (*Ber.*, **21**, 1299), that the difficulty with the monalkyl-deoxybenzoïns form hydroximes increases with ›lecular weight; thus benzyl-deoxybenzoïn only yielded a hydr- when heated with hydroxylamine hydrochloride at 150—160°, ment by which our compound is totally resinised.

or Meyer has shown (*Ber.*, **21**, 1293) that methyldeoxybenzoïn with nitrous acid, eliminating benzoic acid, and yielding aceto- ıoxime. Following this analogy, we treated *p*-desylphenol with acid, hoping to obtain *p*-hydroxybenzophenonoxime and benzoic ut no action could be observed.

ation experiments gave inconclusive results. With alkaline per- ıate, only benzoic acid was obtained, whilst chromium trioxide c acid solution converted the compound into a reddish-brown, allisable substance.

ılso examined the action of concentrated sulphuric acid on ›s of benzoïn with various other phenols: thus, with thymol, hol, resorcinol, and quinol. In every case there appeared to ction, manifested by an intense coloration which neither the nor the phenol alone yielded with sulphuric acid; but the s of the reactions were uncrystallisable resins, which were not examined.

oregoing investigation was commenced by one of us in con- with Mr. F. B. Guthrie, to whom are due the preparation of henol itself and its monacetyl-derivative, and the establishing composition of these compounds. Mr. Guthrie's departure s country to fill a post in the Colonies prevented him from ng the work.

College of Science, London.

LXVIII.—*Paraxylenesulphonic Acids.*

By GERALD T. MOODY, D.Sc., Demonstrator in the Chemical Department, City and Guilds of London Institute, Central Institution, and T. G. NICHOLSON.

THE paraxylene used in the preparation of the compounds described in this paper was obtained in part from Kahlbaum's crude xylene, and in part from paraxylene supplied by the same firm. The purity of each specimen was determined by introducing some of it into a small tube surrounded by a mixture of ice and salt. If it seemed desirable, the bulk of the hydrocarbon was frozen and carefully freed from any adhering liquid by pressure on a well-cooled filter pump. Every sample used melted constantly at 15°.

Dibromoparaxylene, 1 : 2 : 4 : 5-$C_6H_2(CH_3)_2Br_2$.

This compound has been described by Jannasch (*Ber.*, **18**, 358) and O. Jacobsen. To prepare it, 90 grams of paraxylene were placed in an 80-ounce flask together with a little iodine, and 270 grams of bromine slowly added from a separating funnel, the operation taking 12 hours. By this means undue heating was avoided and the hydrogen bromide was evolved in a gentle and regular stream. After the addition of the bromine, the contents of the flask were allowed to remain for 24 hours, and the solid, red-coloured mass was then shaken, first with a warm solution of potash to remove the iodine and excess of bromine, and then repeatedly with warm and cold water. The product was quite solid at ordinary temperatures, and of a pale-yellow colour. On being pressed on the filter pump, scarcely any oil was obtained, and the solid, after one crystallisation from alcohol, melted constantly at 74°. An analysis gave the following result :—

0·204 gram gave 0·286 gram silver bromide and 0·003 gram silver.

	Calculated for $C_6H_2(CH_3)_2Br_2$.	Found.
Br........	60·60 per cent.	60·29 per cent.

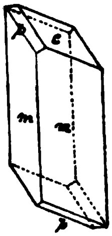
The substance, however, does not agree in crystalline form with the description given by Jacobsen, who states that it crystallises from alcohol in the form of thin plates, and that these, on remaining in the mother liquor for a week, change to crystals which appear to be regular octahedra, but in reality belong to the triclinic system. We could find no indication of this change in the form of the crystals, even when they were allowed to remain in the mother liquor for some weeks. On allowing a drop of the alcoholic solution to evaporate on a slide, long, needle-shaped prisms were obtained; on rapidly cooling the solution, flat, short prisms were formed; and, on allowing the solution to evaporate slowly, long, yellowish, transparent prisms were obtained, and these furnished the following crystallographic characters:—

Crystalline system. Monosymmetric—

$$a : b : c = 0\cdot8049 : 1 : 0\cdot6208.$$

$$\beta = 47^\circ\ 26'.$$

Fig. 1.



Forms observed—

$m = \{110\}$.
$c = \{001\}$.
$p = \{\bar{1}11\}$.

		Observed.	Calculated.
mm.......	$110 : 1\bar{1}0$	61° 19′	—
mc	$110 : 001$	54 25	—
cp........	$001 : \bar{1}11$	56 44	—
mp	$\bar{1}10 : \bar{1}11$	68 48	68° 51′

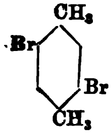
The crystals are often terminated at one end by the face *c*, and at the other by a face of the form *p*.

The optic axes lie in the plane of symmetry 010; through the faces *m*, the direction of extinction makes an angle of 37° with the edge *mm*.

There is a strong dispersion.

Sulphonation of Dibromoparaxylene.

On substituting methyl for bromine in dibromoparaxylene, Jannasch obtained durene; consequently the former has the constitution



and can, therefore, furnish only one monosulphonic acid. 40 grams of the compound were introduced into a dry flask with 100 grams of 20 per cent. SO_3 anhydrosulphuric acid, and the mixture was heated at 80° in a water-bath. The bromine compound readily dissolves, and no charring takes place so long as the temperature does not rise above 85°. On cooling, the product became solid, but readily dissolved on treatment with water; the solution, on concentration, yielding a considerable crop of foliaceous crystals, and a further quantity of these was obtained on evaporation of the mother liquor. On recrystallisation from water, a mass of beautiful, silky needles which melt with decomposition at 151° was formed.

Dibromoparaxylenesulphonic acid differs from its isomeride, dibromometaxylenesulphonic acid [$Me_2 : SO_3H : Br_2 = 1 : 3 : 2 : 4 : 6$], in respect to its stability and power to resist hydrolysis; for a solution of the acid containing free sulphuric acid may be evaporated without regeneration of dibromoparaxylene. Under similar circumstances, the metaxylenesulphonic acid is rapidly hydrolysed.

Barium Dibromoparaxylenesulphonate, $[C_6H(CH_3)_2Br_2 \cdot SO_3]_2Ba$.

This salt is obtained from the sulphonic acid by neutralising it with a sludge of barium carbonate and exhausting with boiling water. It crystallises from the hot aqueous solution in very thin, gleaming scales or flat needles, and is only very sparingly soluble in water. The salt is anhydrous, as shown by the following analyses:—

I. 0·1880 gram of the air-dried salt did not lose in weight on heating for four hours at 150°; at a higher temperature, it carbonised; and gave 0·0555 gram of barium sulphate.

II. 0·2935 gram did not lose in weight on heating for three hours at 140°; the crystals maintained their shape; and gave 0·082 gram of barium sulphate.

	Calculated for $[C_6H(CH_3)_2Br_2 \cdot SO_3]_2Ba$.	Found.
I	16·64 per cent.	17·34 per cent.
II	— „	16·42 „

Sodium Dibromoparaxylenesulphonate, $C_6H(CH_3)_2Br_2\cdot SO_3Na + H_2O$.

This salt, prepared from the above-described barium salt, or precipitated from a solution of the sulphonic acid by sodium carbonate, appears to be amorphous, but really crystallises in microscopic needles. It is only very slightly soluble in cold water, but dissolves more readily in hot water.

I. 0·5375 gram of the air-dried salt lost 0·0280 gram on heating for two hours at 180°.

II. 0·2725 gram gave 0·048 gram sodium sulphate.

	Calculated for $C_6H(CH_3)_2Br_2SO_3Na$.	Found.
Water	4·68 per cent.	(I) 5·21 per cent.
Sodium	5·99 „	(II) 6·5 „

Dibromoparaxylenesulphonic Chloride, $C_6H(CH_3)_2Br_2\cdot SO_2Cl$.

This compound was obtained by treating the dried sodium salt with phosphorus pentachloride. It is very soluble in benzene, from which it crystallises badly, and on spontaneous evaporation of a solution in light petroleum forms stellate groups of flat needles which melt at 78—79°. It crystallises best from alcohol and from acetic acid in the form of flat needles without terminations, having a pair of faces showing straight extinction. These faces are perpendicular to a bisectrix, and the optic axial plane is perpendicular to the length of the needles, the axial angle being very large. No measurements are possible.

0·205 gram, on burning with lime, gave 0·293 gram of silver haloïd compound.

	Calculated for $C_6H(CH_3)_2Br_2\cdot SO_2Cl$.	Percentage of silver haloïd compound found.
AgCl : 2AgBr	143·30	143·43

Dibromoparaxylenesulphonamide, $C_6H(CH_3)_2Br_2\cdot SO_2NH_2$.

This compound was most conveniently prepared by adding aqueous ammonia to a solution of the sulphonic chloride in dilute alcohol, and warming the mixture. On cooling, the sulphonamide separates in thin, pearly plates, almost insoluble in absolute alcohol and in water, and which melt at 198°. When a solution in acetic acid is allowed to evaporate spontaneously, the substance crystallises in thin, colourless, rhombic-shaped plates, with a plane angle of about 60°, and having their edges modified. The habit closely resembles that of selenite. The extinction is perpendicular to one edge, and the plates appear to be perpendicular to a bisectrix, the axial plane being perpendicular to the same edge. The cleavage is perfect, parallel to the surface of the plates; there is also an imperfect cleavage at right angles to this and inclined at about 24° to the axial plane, so that it nearly bisects the obtuse angle of the rhomb. No other measurements were possible.

Reduction of Sodium Dibromoparaxylenesulphonate.

In order, if possible, to isolate a monobromoparaxylenesulphonic acid, two lots of sodium dibromoparaxylenesulphonate, each weighing about 10 grams, were separately dissolved in a large quantity of water and treated with 1 per cent. sodium amalgam, in quantity slightly in excess of that required to remove 1 atom of bromine. The amalgam was added in small quantities at a time, so that the operation of reduction took about three weeks. The solutions were separated from the mercury, nearly neutralised with sulphuric acid, and slowly evaporated. A quantity of the unreduced sodium salt first crystallised out and was filtered off. The liquid was then reduced to a smaller bulk and treated with alcohol, whereby a quantity of sodium sulphate was thrown out of solution. On further evaporation, a crop of crystals was obtained which, after treatment with charcoal and recrystallisation from water, formed a mass of beautiful, colourless plates. A few of these were converted into sulphonamide by treatment with phosphorus pentachloride and with ammonia, and furnished thereby a compound crystallising in needles melting at 147—148° (compare Jacobsen, *Ber.*, **10**, 1009; **11**, 22; and *Annalen*, **136**, 305), which proved the crystals to be *sodium paraxylenesulphonate*. As no crystallographic measurements of this substance have been previously published, and as such are desirable for comparison with those of isomeric compounds, the following description is given:—

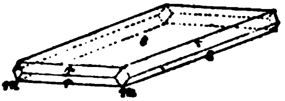
Sodium Paraxylenesulphonate.

$C_6H_3(CH_3)_2 \cdot SO_3Na$.

Crystalline system. Orthorhombic—

$$a : b : c = 1{\cdot}0767 : 1 : 1{\cdot}4882.$$

Fig. 2.



ns observed—

$$c = \{001\}.$$
$$r = \{011\}.$$
$$s = \{101\}.$$
$$m = \{110\}.$$

		Observed.	Calculated.
cs	001 : 101	54° 7′	—
cr	001 : 011	56 6	—
sr	101 : 011	70 56	70° 55′
cm	001 : 110	90 0	90 0
mm	110 : $\bar{1}$10	85 51	85 46½

substance was crystallised from water.

crystals consist of colourless, rectangular plates, having their evelled (Fig. 2).

age.—Imperfect parallel to 100 and 010.

optic axes lie in the plane 001, and the axis *a* is the acute x.

louble refraction is weak; negative; $\rho < v$.

axial angle in air—

$2E_a$ = 27° 18′ for lithium light.
= 27 46 „ sodium „
= 28 53 „ thallium „

Reduction of Dibromoparaxylenesulphonamide.

g failed to obtain the monobromoparaxylenesulphonic acid eduction of sodium dibromoparaxylenesulphonate in aqueous attempts were made to produce it by reduction of the corng sulphonamide in ethereal-alcoholic solution, by sodium 1. After reduction, however, the solution, on fractional sation, furnished a considerable quantity of unreduced sulde and, finally, a substance crystallising in minute scales not melt at 260°, and char at a slightly higher temperature. compound contains neither nitrogen, bromine, nor sulphur, rhaps a tetramethyldiphenyl.

ır intention to further investigate the substance, and we wish e to ourselves the right of examining the behaviour, on reof other substituted sulphonamides.

Summary.

paper the error made by Jacobsen in respect to the crysıy of dibromoparaxylene is rectified, and the sulphonic acid erivatives of this compound are described.

We have pleasure in expressing our obligations to Mr. H. A. Miers, M.A., Instructor in Crystallography at, and to Mr. W. J. Pope, Student in the Chemical Department of the Central Institution, for the crystallographic and optical determinations.

LXIX.—*Action of Phosphoric Anhydride on Fatty Acids.* Part II.

By F. Stanley Kipping, Ph.D., D.Sc.

It was shown in a paper communicated to the Society a short time ago (Trans., 1890, 532), that stearone and dihexyl ketone can be most conveniently prepared by treating stearic acid and heptylic acid respectively with phosphoric anhydride at a suitable temperature, the reaction which takes place being expressed by the equation

$$2R{\cdot}COOH = R_2CO + CO_2 + H_2O.$$

As, in both cases, the yield of ketone is good and the product is easily obtained in a pure condition, it was anticipated that other ketones of the general formula R_2CO might be obtained in a similar manner.

The investigation has now been extended to lauric and palmitic acids, with results that completely bear out this anticipation. Lauric acid is decomposed by phosphoric anhydride at 210—230°, the yield of laurone, $(C_{11}H_{23})_2CO$, under suitable conditions being about 38 per cent. of the theoretical; with palmitic acid, the reaction takes place at 180—200°, and about 50 per cent. of the theoretical quantity of palmitone, $(C_{15}H_{31})_2CO$, is obtained; the isolation of the ketone is easy of accomplishment in both cases, so that the methods detailed below are suitable for their preparation.

Having at my disposal considerable quantities of these two ketones, I have prepared from them, without difficulty, the secondary alcohols $(C_{11}H_{23})_2CH{\cdot}OH$ and $(C_{15}H_{31})_2CH{\cdot}OH$, the acetates of these alcohols, and the oximes $(C_{11}H_{23})_2C{:}N{\cdot}OH$ and $(C_{15}H_{31})_2C{:}N{\cdot}OH$; these compounds all crystallise well except dipalmitylcarbinyl acetate, which seems to be amorphous.

Experiments are being carried out with various acids, both of the fatty and aromatic series; some of the lower fatty acids, caproic acid for example, are readily decomposed by phosphoric anhydride, but the conditions under which a satisfactory yield of ketone is obtained have yet to be determined. The behaviour of a mixture of two acids with phosphoric anhydride is also being investigated, as it seems ıble that this reaction may lead to the formation of mixed .es.

Preparation of Laurone, $(C_{11}H_{23})_2CO$.

ıric acid is not so readily decomposed by phosphoric anhydride ı other fatty acids which have been investigated; at 180° the ı is extremely slow, and even at 210° the evolution of carbonic lride is not very rapid, but at about 220° the acid is readily ıposed.

· the preparation of laurone, the following method has been found e good results:—Pure dry lauric acid (10 grams) is heated to 220° in a tall beaker, placed on a sand-bath or in a metal-bath, ıosphoric anhydride is gradually added, in small portions at a with constant stirring; a considerable development of heat , the temperature rising to about 230°, and the mixture soon a brownish-black, carbonic anhydride being evolved with scence. The addition of phosphoric anhydride is continued, nperature being kept at about 230°, until a fresh portion causes ıher evolution of gas; the beaker is then removed from the bath contents allowed to cool.

whole operation, after the acid has acquired the requisite tem-·e, occupies only three or four minutes; and about 7 grams ıphoric anhydride, a quantity which is considerably in excess theoretical, must be used to decompose the whole of the

lark, waxy product is stirred up with water and then heated to boiling with excess of potash, in order to remove the phos-ıcid and any unchanged lauric acid which might be present; irring well for a few minutes, the mixture is allowed to cool, ı the laurone and resinous products collect at the surface of ıline liquid in the form of a dark-brown oil, which solidifies ing. The waxy cake is separated from the alkaline liquid ically, washed on a filter with hot water, transferred, together ıe filter-paper, to a flask of about 500 c.c. capacity, and d with boiling moderately dilute methylated spirits. The . of a few pieces of filter-paper to absorb the oily impurities ıd as advantageous in extracting the laurone, as is the case eparation of stearone; the alcoholic solution then remains clear, be simply decanted from the paper and insoluble residue. ·one, which is deposited from the alcoholic solution on cool-ıparated by filtration and the filtrate is again employed for ıg the residue in the flask; in this way, employing about of methylated spirits, the whole of the ketone can be l in three, or at the most four, operations, the last extract being diluted with water, in order to ensure complete precipitation from the cold solution.

The yield of crude laurone, dried first on a porous plate, and then at 100°, is 3·2 grams from 10 grams of the acid, which is nearly 38 per cent. of the theoretical quantity. The crude product melts at about 67°, and is almost pure, provided the alcohol employed in extracting it is sufficiently dilute; after crystallising it twice from boiling alcohol, it is obtained in colourless, waxy plates melting at 69°.

The analysis of a portion of the pure ketone, dried over sulphuric acid, gave the following result:—

0·1674 gram of substance gave 0·4996 gram of CO_2 and 0·2048 gram of H_2O.

	Calculated for $C_{23}H_{46}O$.	Found.
C	81·65 per cent.	81·39 per cent.
H	13·61 „	13·59 „
O	4·74 „	5·02 „

Laurone was first prepared by Overbeck (*Annalen*, **84**, 289), by the distillation of calcium laurate, and subsequently by Krafft (*Ber.* **15**, 1712), by distilling barium laurate with calcium oxide, under a pressure of 10—15 mm. The melting point of the ketone is 66° according to Overbeck, whereas Krafft found it to be 69°; neither author states what the yield is by the process he employed, but, judging from analogous cases, it is probably less than by the method described above.

Laurone crystallises from hot alcohol, in which it is moderately easily soluble, in large, colourless, waxy plates, melts at 69°, and distils at a high temperature with only slight decomposition when heated in small quantities; it is readily soluble in chloroform, benzene, light petroleum, boiling ether, and hot glacial acetic acid, but only sparingly in cold acetic acid, and almost insoluble in cold alcohol; on the addition of methyl alcohol to a cold ethereal solution, it is precipitated in ill-defined crystals. It can be easily converted into the corresponding secondary alcohol, and it combines readily with hydroxylamine.

Considerable quantities of dark-coloured bye-products are obtained when lauric acid is treated with phosphoric anhydride as described above, and it has not been found possible to avoid their formation, which seems to be due to the action of the anhydride on the laurone produced in the reaction; when the quantity of phosphoric anhydride employed is less than about 7 grams, the actual yield of ketone is diminished, but a larger or smaller quantity of acid, according to the amount of anhydride used, remains unchanged, and can be recovered from the alkaline solution, so that the theoretical yield of ketone remains about the same.

Laurone Oxime, $(C_{11}H_{23})_2C{:}N{\cdot}OH$.

The oxime of laurone can be prepared by adding a dilute methyl alcoholic solution of hydroxylamine hydrochloride (0·6 gram) and potash (1·2 gram) to a warm solution of the pure ketone in methyl alcohol, keeping the mixture for four hours at the ordinary temperature, and then heating at 60—70° for about half an hour. The solution is finally heated to boiling, filtered from the crystals of potassium chloride, and the filtrate carefully acidified with warm dilute hydrochloric acid; the oxime, which is deposited in colourless crystals on cooling, is separated by filtration, recrystallised from boiling alcohol, and dried on a porous plate.

A nitrogen determination made with a portion of the pure substance prepared in this way gave the following result:—

0·2225 gram of substance gave 8·9 c.c. of nitrogen measured at 17° under a pressure of 735 mm.

	Calculated for $C_{23}H_{47}NO$.	Found.
N	4·0 per cent.	4·5 per cent.

Laurone oxime crystallises from hot dilute alcohol in long, slender, colourless needles, melting at 39—40°; it dissolves freely in cold glacial acetic acid, from which it is precipitated in plates on the addition of water, and it is readily soluble in benzene and light petroleum, but only sparingly in cold alcohol, and seemingly insoluble in water and concentrated alkalis.

Dilauryl Carbinol, $(C_{11}H_{23})_2CH{\cdot}OH$.

This secondary alcohol can be obtained without difficulty by reducing laurone with sodium and water. For this purpose, the pure ketone (2 grams) is dissolved in warm ether, and the ethereal solution is poured into a large bottle, containing about 100 c.c. of concentrated soda and provided with a reflux condenser; a large excess (about 5 grams) of the theoretical quantity of sodium is then introduced, in small portions at a time, any considerable rise in temperature being avoided by surrounding the bottle with cold water. As soon as the whole of the sodium has dissolved, the ethereal solution is separated, the alkali extracted once with ether, the combined extracts dried over potassium carbonate and evaporated.

The colourless oil obtained in this way immediately solidifies on cooling to a wax-like mass, and can be purified by recrystallisation from hot methyl alcohol.

The analysis of the pure alcohol, dried at 100°, gave the following result:—

0·1816 gram of substance gave 0·5255 gram of CO_2 and 0·2198 gram of H_2O.

	Calculated for $C_{23}H_{48}O$.	Found.
C	81·17 per cent.	81·08 per cent.
H	14·12 ,,	14·16 ,,
O	4·71 ,,	4·74 ,,

Dilauryl carbinol separates from hot ether in well-defined, colourless plates, and from boiling methyl alcohol in peculiar fern-like crystals, melting at 75—76°. It is readily soluble in cold benzene, chloroform, light petroleum, and hot glacial acetic acid, but only moderately easily in hot alcohol and cold glacial acetic acid and is insoluble in water.

Dilaurylcarbinyl Acetate, $(C_{11}H_{23})_2CH\cdot OAc$.

For the better characterisation of the alcohol, it was converted into the acetate by boiling it for about eight hours with a large excess of acetic anhydride in a flask provided with a reflux apparatus; on cooling, the ethereal salt is deposited from the solution in colourless crystals, mixed, however, with a small quantity of unchanged alcohol The two compounds can be easily separated by dissolving the mixture in a considerable quantity of boiling methyl alcohol and allowing the solution to cool slowly; almost the whole of the dilauryl carbinol crystallises from the solution and is separated by filtration, the acetate, which remains dissolved, being then precipitated by diluting with water; the compound, purified in this way, melted at 34—35°, and its melting point did not alter on recrystallisation.

The following result was obtained on analysis of a portion of the pure ethereal salt, dried at 100°:—

0·1818 gram of substance gave 0·5217 gram of CO_2 and 0·2174 gram of H_2O.

	Calculated for $C_{25}H_{50}O_2$.	Found.
C	78·53 per cent.	78·26 per cent.
H	13·09 ,,	13·29 ,,
O	8·38 ,,	8·45 ,,

Dilaurylcarbinyl acetate crystallises from dilute methyl alcohol in less plates, melts at 34—35°, and is much more readily soluble hyl alcohol than the alcohol from which it is derived. It is r soluble in cold benzene, but only moderately in cold glacial acid, and very sparingly in cold acetic anhydride. It is y hydrolysed by boiling alcoholic potash, being reconverted lauryl carbinol.

Preparation of Palmitone, $(C_{15}H_{31})_2CO$.

the preparation of this ketone, pure palmitic acid should be ed, the process being carried out in a manner similar to that ed in the case of laurone, except that the temperature required omposition is not so high.

itic acid (10 grams) is heated at 200—210° in a beaker placed id-bath, and the phosphoric anhydride added in small portions e with constant stirring; a considerable development of heat and rapid effervescence sets in owing to the liberation of anhydride, the mixture at the same time becoming rapidly in colour. It was found convenient to employ sufficient ric anhydride to decompose the whole of the acid, as, if this is e, the subsequent isolation of the ketone is rather more ome; for this purpose, about 6 grams of the anhydride are , the end of the reaction being shown by the cessation of ence on the addition of a fresh portion. The dark-brown is allowed to cool, freed from phosphoric acid exactly as d in the preparation of laurone, and the residue extracted ree times with boiling dilute methylated spirit, the solvent sed over and over again. The ketone, which is deposited alcoholic solution, on cooling, in the form of yellowish flakes, ted by filtration and dried on a porous plate. The crude prepared in this way, is almost pure and melts at about 78°; 3 grams of crude ketone, dried at 100°, are obtained from of palmitic acid, a yield which is just over 50 per cent. of retical. After recrystallisation from boiling alcohol, it is in colourless plates melting at 82—83°.

alysis of the pure compound, dried at 100°, gave the follow- :—

gram of substance gave 0·5868 gram of CO_2 and 0·2388 of H_2O.

	Calculated for $C_{31}H_{62}O$.	Found.
C	82·66 per cent.	82·32 per cent.
H	13·78 ,,	13·65 ,,
O	3·55 ,,	4·03 ,,

Palmitone has been previously prepared by Piria (*Annalen*, **82**, 249) and others, and more recently, by an improved process, by Krafft (*Berichte*, **15**, 1714), who obtained it by the distillation of barium palmitate with calcium oxide under greatly reduced pressure; the yield is not given in Krafft's paper, but it is doubtless considerably less than 50 per cent. of the theoretical.

Bye-products are obtained in the preparation of palmitone in the manner described above; they seem to be of the same nature as those formed in the preparation of laurone and stearone, but have not yet been examined very closely.

Palmitone Oxime $(C_{15}H_{31})_2C:N\cdot OH$.

Palmitone does not seem to combine with hydroxylamine at the ordinary temperature; the oxime can, however, be obtained by boiling the ketone for about 1½ hours with a large excess of hydroxylamine hydrochloride and excess of potash in alcoholic solution. The crystals of potassium chloride are then separated by filtration, and the filtrate is allowed to cool slowly; the oxime, which is deposited from the solution in colourless crystals, is washed well with cold dilute methyl alcohol, recrystallised from this solvent, and dried on a porous plate.

The compound, purified in this way, showed signs of softening at 57—58°, and melted completely at 59°; it seemed quite homogeneous under the microscope.

A nitrogen determination with a portion of the substance which had been dried over sulphuric acid gave the following result:—

0·2226 gram of substance gave 6·7 c.c. of nitrogen, measured at 14° under a pressure of 745 mm.

	Calculated for $C_{31}H_{63}NO$.	Found.
N	3·0 per cent.	3·4 per cent.

Palmitone oxime separates from boiling alcohol in fern-like crystals, and from hot glacial acetic acid in groups of needles. It dissolves freely in cold benzene and light petroleum, but is only sparingly soluble in boiling glacial acetic acid and alcohol, almost insoluble in the cold solvents, and insoluble in soda.

Dipalmityl Carbinol $(C_{15}H_{31})_2CH\cdot OH$.

As palmitone is only sparingly soluble in cold ether, dipalmityl carbinol cannot be conveniently prepared by reducing the ketone with sodium and water as described in the case of dilauryl carbinol, an be easily obtained in the following manner:—The pure s dissolved in boiling alcohol in a flask provided with a reflux er, and a large excess over and above the theoretical quantity m is added in small portions at a time, the solution being its boiling point. The whole of the sodium being dissolved, tion is diluted with warm water and allowed to cool; the n-product, which is gradually deposited in colourless crystals, ted by filtration, washed well with warm water to free it from nd recrystallised from boiling alcohol.

nalysis of the pure alcohol, dried at 100°, gave the following

gram of substance gave 0·5577 gram of CO_2 and 0·2368 m of H_2O.

	Calculated for $C_{31}H_{64}O$.	Found.
C........	82·30 per cent.	82·15 per cent.
H........	14·16 „	14·21 „
O........	3·54 „	3·64 „

nityl carbinol crystallises from boiling alcohol in colourless, dles or plates, melts at 84—85°, and distils under the ordi- ssure with only very slight decomposition when it is heated quantities. It is readily soluble in hot ether, light petroleum, benzene, but only moderately easily in hot alcohol and lcohol, and insoluble in water.

Dipalmitylcarbinyl Acetate, $(C_{15}H_{31})_2CH{\cdot}OAc$.

lmityl carbinol and the ketone from which it was prepared y little in percentage composition and as, moreover, the oints of the two compounds lie within about 5° of one t seemed necessary to prepare the acetate of the alcohol in btain some more conclusive proof that the compound de- ove is, in reality, dipalmityl carbinol.

purpose, the pure alcohol, melting at 84—85°, was boiled 3 hours with a large excess of acetic anhydride, in a flask vith a reflux apparatus, and the solution then allowed to product, which separates almost immediately as an oil, radually solidifies, was recrystallised from boiling alcohol, in hot ether, reprecipitated by adding methyl alcohol, and porous plate. It is thus obtained in the form of a colour- lar, seemingly amorphous powder melting at 47—49°. The the dry substance gave the following result :—

0·1894 gram of substance gave 0·5498 gram of CO_2 and 0·2250 gram of H_2O.

	Calculated for $C_{33}H_{66}O_2$.	Found.
C	80·16 per cent.	79·70 per cent.
H........	13·36 „	13·20 „
O........	6·48 „	7·10 „

Dipalmitylcarbinyl acetate is readily soluble in cold ether, benzene, and hot amyl alcohol, and moderately easily in hot light petroleum, but only sparingly in boiling methyl alcohol, and insoluble in water. When boiled with alcoholic potash, it is quickly hydrolysed, being reconverted into dipalmityl carbinol.

Heriot Watt College,
Edinburgh.

LXX.—*An Investigation of the Conditions under which Hydrogen Peroxide is formed from Ether.* (Second Notice.)

By Wyndham R. Dunstan and T. S. Dymond.

In a paper recently published in the Journal (Trans., 1890, 574), we have drawn attention to the conflicting statements which have been recorded respecting the formation of hydrogen peroxide from ether, and we have pointed out that the whole question stands in need of re-investigation, owing to the circumstance that there is no evidence that pure ether has been employed by previous observers, who have either omitted all reference to the manner in which the ether employed by them was purified, or have described methods which are not adequate for the purpose of purifying a liquid which is particularly difficult to obtain in a pure state. We have described in detail the plan which we have found successful for this purpose. Employing such purified ether, we have determined whether hydrogen peroxide can be formed from it under three distinct conditions, namely (1), by the action of ozone and subsequently of water; (2) by the slow and imperfect oxidation of ether by air at the lowest possible temperatures (200—300°); and (3) by the action of light (diffused daylight and electric light) in the cold. Under the two first-named circumstances, we were able to demonstrate the production of hydrogen peroxide; but we failed to observe its formation except in impure specimens, during the exposure of ether in contact with water and air to diffused daylight or electric light. We were unable to command in London at the time when our experiments were made any duration of sunlight, or indeed to obtain sunlight which had not been greatly impoverished in its passage through the atmosphere. Although it then seemed to us unlikely that different results would be obtained in bright sunlight, yet, as the experiments which have been recorded by some previous observers on the formation of hydrogen peroxide from ether had been made under these circumstances, we took the opportunity last May of making at Oxford a series of experiments in which pure ether in contact with oxygen and water was exposed in bright sunlight. Several specimens of the ether were enclosed in long glass tubes having a capacity of rather more than half a litre. About 50 c.c. of water and the same quantity of ether having been introduced into the tube, the air contained in it was replaced by oxygen, which would presumably lead to the formation of a larger quantity of hydrogen peroxide than the same volume of air; the tubes were then hermetically closed. Duplicate specimens of ether, water, and oxygen were also exposed in the almost colourless (slightly greenish) Winchester bottles which we had employed in the previous series of experiments. For rather more than four months (May 16th to September 29th) the tubes and bottles were exposed to sunlight in the open air on a verandah having a southern aspect. By their side was placed a sealed tube rendered opaque by thickly coating it with black varnish, and likewise containing ether, water, and oxygen, so that we might be able by an examination of the contents of this tube after exposure to ascertain whether the temperature attained by it in sunlight would alone be sufficient to produce hydrogen peroxide.

Through the kindness of Mr. E. J. Stone, F.R.S., the Radcliffe Observer, we are enabled to state the sunshine record for the months of June, July, August, and September, and also the readings of a black-bulb thermometer exposed *in vacuo*, these observations having been made at the Radcliffe Observatory, Oxford, close to the place where our experiments were conducted.

During June, 139 hours of sunshine were recorded; during July, 150 hours; during August, 171 hours; during September, 150 hours. The highest readings of a black-bulb thermometer exposed to sunlight in a vacuum were: in June, 52·2°; in July, 56·1°; in August, 54·8°; in September, 50·8°.

The results we have obtained prove that hydrogen peroxide is produced from pure ether by exposure to bright sunlight in contact with water and oxygen. The liquids enclosed in tubes and those contained in the bottles alike afforded the characteristic reaction with acidified chromate with the exception of that contained in the darkened tube, which, although it apparently did not contain hydrogen peroxide, nevertheless liberated iodine from potassium iodide. In no case did the amount of hydrogen peroxide exceed 0·1 per cent. Accompanying the hydrogen peroxide, we found small quantities of the oxidation products of ether, among them being aldehyde and acetic acid. The conditions under which these experiments were made differ from those of the previous series in three respects: firstly, in the substitution of oxygen for air; secondly, in the existence of a higher temperature; and, thirdly, in the employment of bright sunlight instead of the electric light. In considering to which of these three conditions the different result may be ascribed, it seems improbable that the use of oxygen instead of air can have materially affected the result; it has been proved that the higher temperature alone is incompetent to produce the effect; there remains the difference that whilst in the first series of experiments the electric light acted at a low temperature (10—15°), in the second series bright sunlight acted at a much higher temperature. Now we have already shown that hydrogen peroxide is formed when ether is imperfectly oxidised by heating its vapour with oxygen in such a manner that the products of the change can at once come into contact with cold water. Under the influence of sunlight, it would appear that the same action takes place, but at a lower temperature. Since hydrogen peroxide is produced from ether in bright sunlight but not in the electric light, it is probable that the red and not the violet rays of light are operative in producing the change, although further experiments are needed to determine whether the violet and ultra-violet rays may not themselves be competent to produce the same effect, provided that the temperature is higher than that which obtained during our experiments with the electric light. The formation of only small quantities of hydrogen peroxide would appear to be due to its destruction by some of the oxidation products of ether which are formed simultaneously.

All these facts point to the conclusion that the formation of hydrogen peroxide is the accompaniment of the slow oxidation of ether. Having regard to the fact recorded in our first paper, that ozone is absorbed by pure ether, forming, according to Berthelot, ethyl peroxide, and that the solution affords hydrogen peroxide when mixed with water, it seems possible that the production of hydrogen peroxide by the slow oxidation of ether in contact with water may be due to the same process of chemical change, and that the oxygen unites with ether forming a compound which is decomposed by water with the production of hydrogen peroxide. Another explanation has, however, been suggested by Dr. Arthur Richardson, to which we have already referred in our previous paper. It supposes that under the influence of sunlight water is oxidised to hydrogen peroxide by the oxygen gas which is in contact with it, the ether remaining unchanged, and acting only as a preservative of the hydrogen peroxide; indeed, Dr. Richardson claims to have proved that water acidulated with sulphuric acid combines with oxygen under the influence of sunlight, forming hydrogen peroxide. We have already recorded our failure to observe the formation of hydrogen peroxide from acidulated water when exposed at a low temperature to the electric light. We have since repeated the experiments in bright sunlight with pure water containing 1 per cent. of pure redistilled sulphuric acid. The acidulated water (50 c.c.) was sealed with oxygen in a glass tube and exposed at the same time and under exactly the same conditions as the tubes of ether referred to above. After a period of four months, we were unable to detect any hydrogen peroxide in the liquid, which reacted neither with chromate nor with potassium iodide.

Since our first paper was published, a more detailed account of Dr. Richardson's experiments has appeared (*British Association Report*, 1889) than that which is contained in the abstract in the *Proceedings* of this Society (1889, 134). From this we learn that the amount of hydrogen peroxide stated to be formed from acidulated water never exceeded 0·0019 per cent., and often ranged between 0·0001 and 0·0006 per cent. Apparently the only evidence that hydrogen peroxide exists in the liquid is its reducing action on permanganate, evidence which appears to us to be quite inconclusive. Moreover, it is well known that dilute acidified solutions of hydrogen peroxide possess considerable stability, and some explanation is required to account for the presence of such minute quantities as those mentioned in a liquid which is known to favour the continued existence of the substance.

LXXI.—CONTRIBUTIONS FROM THE LABORATORIES OF THE HERIOT WATT COLLEGE, EDINBURGH.

On Berberine. Part II.*

By W. H. Perkin, Jun., Ph.D., F.R.S.

CONTENTS.

PAGE
Introduction 993
Constitution of Anhydroberberilic and Berberilic Acids 998
Examination and Constitution of Berberal 1000
Constitution of Berberine 1003

Oxidation of Berberine with Potassium Permanganate 1010

Table showing the Separation of the Substances obtained by the Oxidation of Berberine 1014

ω-Amidoethylpiperonylcarboxylic Anhydride, $C_{10}H_9NO_3$ 1013
1. Acetylamidoethylpiperonylcarboxylic Anhydride, $C_{12}H_{11}NO_4$ 1016
2. Amidoethylbromopiperonylcarboxylic Anhydride, $C_{10}H_8BrNO_3$ 1017
3. Nitrosoamidoethylpiperonylcarboxylic Anhydride, $C_{10}H_8N_2O_4$ 1018
4. Hydroxyethylpiperonylcarboxylic Acid, $C_{10}H_{10}O_5$, and its Anhydride, $C_{10}H_8O_4$ 1020
5. Hydroxyethylbromopiperonylcarboxylic Acid, $C_{10}H_9BrO_5$, and its Anhydride, $C_{10}H_7BrO_4$ 1025
6. Hydroxyethylnitropiperonylcarboxylic Anhydride, $C_{10}H_7N_2O_6$ 1027
7. Hydroxyethylcatecholcarboxylic Anhydride, $C_9H_8O_4$ 1027
8. Action of Phosphorus Pentachloride on the Anhydride $C_{10}H_8O_4$; Chlorethylpiperonylcarboxylic Acid, $C_{10}H_9ClO_4$ 1029
9. Methylic Chlorethylpiperonylcarboxylate, $C_{11}H_{11}ClO_4$ 1032
10. Oxyhydrastinine, $C_{11}H_{11}NO_3$ 1034
11. Ethylamidoethylpiperonylcarboxylic Anhydride, $C_{12}H_{13}NO_3$ 1035
12. Phenylamidoethylpiperonylcarboxylic Anhydride, $C_{16}H_{13}NO_3$ 1036

Anhydroberberilic Acid, $C_{20}H_{17}NO_8$, *and its Salts* 1037
1. Methyl Salt of Anhydroberberilic Acid, $C_{21}H_{19}NO_8$ 1039
2. Acetylanhydroberberilic Acid, $C_{22}H_{19}NO_9$ 1041
3. Anhydroberberilic Chloride, $C_{20}H_{16}NClO_7$ 1042
4. Amide of Anhydroberberilic Acid, $C_{20}H_{18}N_2O_7$ 1046
5. Anilide of Anhydroberberilic Acid, $C_{26}H_{22}N_2O_7$ 1047

Berberilic Acid, $C_{20}H_{19}NO_9$, *and its Salts* 1048
1. Dimethyl Salt of Berberilic Acid, $C_{22}H_{23}NO_9$ 1050
2. Action of Heat on Berberilic Acid 1051
3. Hydrolysis of Berberilic Acid: Preparation of ω-Amidoethylpiperonylcarboxylic Acid, $C_{10}H_{11}NO_4$ 1053

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* Part I, Trans., 1889, 63.

PAGE
4. Dibenzoylamidoethylpiperonylcarboxylic Acid, $C_{24}H_{19}NO_6$ 1059
5. Action of Nitrous Acid on Amidoethylpiperonylcarboxylic Acid. Formation of Hydroxyethylpiperonylcarboxylic Acid 1060

Synthesis of Anhydroberberilic Acid.................................... 1061

Berberal, $C_{20}H_{17}NO_7$.. 1062
1. Hydrolysis of Berberal. Preparation of Pseudopianic Acid, $C_{10}H_{10}O_5$ 1064
2. Action of Potassium Hydrate on Pseudopianic Acid. Formation of Veratric Acid, $C_9H_{10}O_4$.................................... 1067
3. Oxime of Pseudopianic Acid, $C_{10}H_{11}NO_5$ 1069
4. Action of Heat on the Oxime of Pseudopianic Acid. Formation of Hemipinimide, $C_{10}H_9NO_4$................................ 1070
5. Oxime of Opianic Acid, $C_{10}H_{11}NO_5$ 1070
6. Reduction of Pseudopianic Acid. Formation of Pseudomeconine, $C_{10}H_{10}O_4$ 1072
7. Pseudomeconinic Acid, $C_{10}H_{12}O_5$ 1073
8. Action of Alkalis on Berberal. Formation of Pseudopianic Acid, $C_{10}H_{10}O_5$; Pseudopianate of Amidoethylpiperonylcarboxylic Anhydride, $C_{20}H_{19}NO_8$, and of Amidoethylpiperonylcarboxylic Anhydride, $C_{10}H_9NO_3$.................................... 1075
9. Action of Phenylhydrazine on Berberal 1077
10. Synthesis of Berberal.. 1079
11. Pseudopianate of Amidoethylpiperonylcarboxylic Anhydride, $C_{20}H_{19}NO_8$.. 1080

Isoberberal, $C_{20}H_{17}NO_7$.. 1081
Opianate of ω-Amidoethylpiperonylcarboxylic Anhydride, $C_{20}H_{19}NO_8$... 1082

Separation of Oxyberberine, Dioxyberberine, and Anhydroberberilic Acid ... 1083
Oxyberberine, $C_{20}H_{17}NO_5$.. 1085
Dioxyberberine, $C_{20}H_{17}NO_6$ 1087
Action of Alkalis on Dioxyberberine.................................... 1089
Berilic Acid, $C_{20}H_{15}NO_8$.. 1091
Hemipinic Anhydride, $C_{10}H_8O_5$...................................... 1094
Hydrastic Acid, $C_9H_6O_6$ 1095
Berberine Hydrogen Sulphite, $C_{20}H_{17}NO_4,H_2SO_3$....................... 1097
Examination of the Mother Liquors of Berberilic Acid and of Berberal.. 1098
Examination of the Aqueous Mother Liquors from the Oxidation of Berberine.. 1105

Introduction.

In a paper communicated to the Society some time since, I showed that berberine, $C_{20}H_{17}NO_4$, when very carefully oxidised with potassium permanganate in alkaline solution, yields, besides hemipinic acid and other simply constituted substances, a number of interesting derivatives, containing the same number of carbon atoms as the alkaloïd itself.

The further study of the oxidation of berberine has led to the isolation of some new compounds still containing 20 carbon atoms, and the exhaustive examination of these has given many results which afford a very clear insight into the constitution of the alkaloïd.

The most important of these derivatives are the following:—

Oxyberberine	$C_{20}H_{17}NO_5$,
Dioxyberberine............	$C_{20}H_{17}NO_6$,
Berberal	$C_{20}H_{17}NO_7$,
Anhydroberberilic acid.....	$C_{20}H_{17}NO_8$,
Berberilic acid	$C_{20}H_{19}NO_9$.

and these, with the exception of the last-named, are derived from berberine by the addition of 1, 2, 3, and 4 oxygen atoms.

Before explaining in detail the methods employed in preparing and separating these compounds, I propose to give a short sketch of the results of the experiments which have thrown the most light on the constitution of berberine. In doing this it will be well to commence with anhydroberberilic acid, as the study of the properties of this substance served as a foundation on which the examination of the other derivatives was based. Anhydroberberilic acid is almost insoluble in aqueous alkalis and alkaline carbonates at ordinary temperatures, but when warmed with dilute sodium hydrate solution it is readily dissolved, yielding a salt of *berberilic acid*:—

$$C_{20}H_{17}NO_8 + 2NaOH = C_{20}H_{17}NO_9Na_2 + H_2O.$$

As the free acid, at temperatures above 170°, is reconverted into anhydroberberilic acid, it was at first supposed that berberilic acid was a bibasic acid, containing two carboxyl groups in the ortho-position, and that anhydroberberilic acid was simply its anhydride; subsequent examination showed, however, that although the latter compound is undoubtedly an anhydride of berberilic acid, it is at the same time itself an acid and not a neutral compound.

In support of this statement the following facts may be mentioned:—

1. Under certain conditions (explained in detail in the experimental part of this paper) anhydroberberilic acid forms salts of the formula $C_{20}H_{16}NO_8M'$.
2. When treated with phosphorus pentachloride, anhydroberberilic is converted into the corresponding acid chloride $C_{20}H_{16}NClO_7$, thus:—

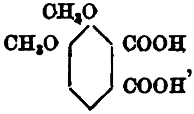
$$C_{20}H_{17}NO_8 + PCl_5 = C_{20}H_{16}NClO_7 + POCl_3 + HCl.$$

From this chloride, the amide $C_{20}H_{16}N(NH_2)O_7$ and the anilide $C_{20}H_{16}N(NH{\cdot}C_6H_5)O_7$ have been prepared.

An insight into the constitution of anhydroberberilic acid was first obtained by the study of berberilic acid, $C_{20}H_{19}NO_9$. This acid is readily obtained by dissolving the anhydro-acid in warm dilute alkalis, and precipitating the alkaline solution with dilute hydrochloric acid; it is a bibasic acid forming salts of the formula $C_{20}H_{17}NO_9M'_2$.

The most interesting salt of this acid is the ammonium salt, $C_{20}H_{17}NO_9(NH_4)_2$, as this when gently warmed or allowed to stand over sulphuric acid in a vacuum, gradually loses half its ammonia, yielding the ammonium salt of anhydroberberilic acid:—

$$C_{20}H_{17}NO_9(NH_4)_2 = C_{20}H_{16}NO_8(NH_4) + H_2O + NH_3.$$

Although only slowly acted on by alkalis, berberilic acid dissolves readily in boiling dilute sulphuric acid, being at the same time decomposed quantitatively into hemipinic acid, , and a new base, $C_{10}H_{11}NO_4$, thus:—

$$C_{20}H_{19}NO_9 + H_2O = \begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COOH\\COOH\end{matrix} + C_{10}H_{11}NO_4.$$

When heated at 180° or digested with strong aqueous potassium hydrate, or even when simply boiled with water for some time, this base loses the elements of a molecule of water, and is converted into its inner anhydride, $C_{10}H_9NO_3$, thus:—

$$C_{10}H_{11}NO_4 = C_{10}H_9NO_3 + H_2O.$$

This important substance is feebly basic, its salts being only stable in the presence of large quantities of acid. By the action of nitrous acid, it is converted into a yellow nitroso-compound, $C_{10}H_8(NO)NO_3$, which, when boiled with dilute caustic soda, rapidly dissolves with evolution of nitrogen, thus:—

$$C_{10}H_8(NO)NO_3 + H_2O = C_{10}H_{10}O_5 + N_2.$$

This substance, $C_{10}H_{10}O_5$, is a monobasic acid, the salts of which are fairly characteristic. When heated to 150° or boiled with water, it readily loses 1 mol. of water and is converted into its inner anhydride, $C_{10}H_8O_4$, thus:—

$$C_{10}H_{10}O_5 = C_{10}H_8O_4 + H_2O.$$

This anhydride is reconverted by dissolution in alkalis into the acid $C_{10}H_{10}O_5$.

Numerous experiments were tried with the object of oxidising this substance to some well known acid, but without success, the compound being either unacted on or else completely destroyed by the oxidising agents employed. When gently fused with potash, the substance yields a mixture of catechol and protocatechuic acid. This reaction affords some clue to the constitution of this series of compounds, as it proves them to be derivatives of orthodihydroxybenzene; as, however, on the other hand, these substances give no reaction with ferric chloride, the absence of hydroxyl groups must be assumed.

When the anhydride $C_{10}H_8O_4$ was heated with hydriodic acid in Zeisel's apparatus (*Monatsh.*, 6, 995), not a trace of methyl iodide was evolved, proving the absence of methoxy-groups; decomposition had, however, evidently taken place, as ether extracted from the residue in the retort a dark coloured substance which gave an intense green coloration with ferric chloride, but could not be obtained in a crystalline condition.

Hydrochloric acid at 170—175° decomposes the compound $C_{10}H_8O_4$, apparently quantitatively, with deposition of carbon and formation of a new compound, $C_9H_8O_4$, thus:—

$$C_{10}H_8O_4 = C_9H_8O_4 + C.$$

This, with ferric chloride, gives the most intense catechol reaction; it also gives a white precipitate with acetate of lead, and reduces both Fehling's solution and ammoniacal nitrate of silver. This decomposition into carbon and a catechol derivative on heating with water or dilute hydrochloric acid is characteristic of piperonyl derivatives* (Fittig, Remsen, *Annalen*, **159**, 139), and the above experiment, therefore, proves that the derivatives obtained from the base $C_{10}H_{11}NO_4$ (including the base itself) must contain the piperonyl group, $CH_2{<}\substack{O\\O}{>}C_6H_4$.

As also, the fact that the two compounds $C_{10}H_{11}NO_4$ and $C_{10}H_{10}O_5$ are readily converted into inner anhydrides proves that they, and therefore their derivatives, must contain two side chains in the ortho-position, the following formulæ may be taken as representing the constitution of these derivatives.

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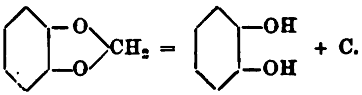
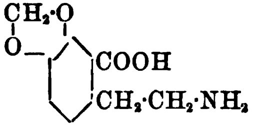
* The nature of this reaction may perhaps be rendered more clear by the partial equation—



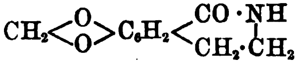
For the sake of brevity, I propose that the group $C_6H_4{<}\substack{O\\O}{>}CH_2$, which occurs in such a large class of compounds, shall be simply called "*piperonyl*."

$C_{10}H_{11}NO_4$ =



= ω-Amidoethylpiperonylcarboxylic acid.*

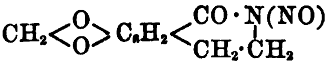
$C_{10}H_9NO_3$



$$= CH_2\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}CO\cdot NH\\ CH_2\cdot CH_2\end{matrix}\right.$$

= ω-Amidoethylpiperonylcarboxylic anhydride.

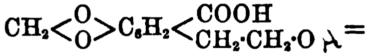
$C_{10}H_8(NO)NO_3$=



$$CH_2\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}CO\cdot N(NO)\\ CH_2\cdot CH_2\end{matrix}\right.$$

= Nitroso-ω-amidoethylpiperonylcarboxylic anhydride.

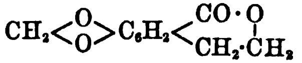
$C_{10}H_{10}O_5$



$$= CH_2\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}COOH\\ CH_2\cdot CH_2\cdot OH\end{matrix}\right.$$

= ω-Hydroxyethylpiperonylcarboxylic acid.

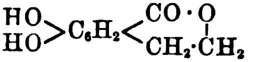
$C_{10}H_8O_4$



$$= CH_2\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}CO\cdot O\\ CH_2\cdot CH_2\end{matrix}\right.$$

= ω-Hydroxyethylpiperonylcarboxylic anhydride.

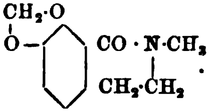
$C_9H_8O_4$



$$= \begin{matrix}HO\\HO\end{matrix}\!>C_6H_2\left<\begin{matrix}CO\cdot O\\ CH_2\cdot CH_2\end{matrix}\right.$$

= ω-Hydroxyethylcatecholcarboxylic anhydride.

Freund and Will (*Berichte*, **20**, 2400), in their researches on hydrastine, describe a substance, oxyhydrastinine, obtained by the action of caustic potash on hydrastinine, which they subsequently prove to have the constitution



If the formulæ assigned to the compounds above be correct, oxyhydrastinine must be a methyl derivative of the compound $C_{10}H_9NO_3$, and in order to confirm these formulæ every effort was made to convert the substance $C_{10}H_9NO_3$ into oxyhydrastinine.

This proved to be extremely difficult, and numerous experiments, extending over several months, failed to bring about the desired result. The transformation was, however, ultimately accomplished in the following way:—

The compound $C_{10}H_8O_4$, when heated with phosphorus pentachloride, is converted into the chloride of ω-chlorethylpiperonylcarboxylic acid, thus:—

$$C_{10}H_8O_4 + PCl_5 = C_{10}H_8O_3Cl_2 + POCl_3,$$

---

* The relative portion of the two pairs of ortho-side chains is very probably that given here, but further experiments are needed before this view can be definitely accepted.

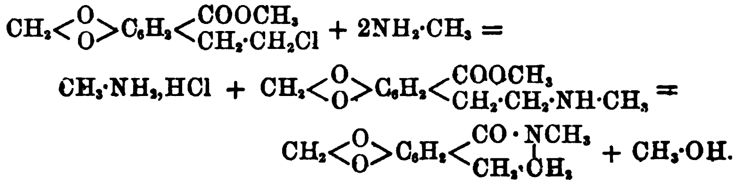
which, when decomposed by water, is converted into the acid $C_{10}H_9O_4Cl$, thus:—

$$C_{10}H_8O_3Cl_2 + H_2O = C_{10}H_9O_4Cl + HCl.$$

This new acid is remarkable for the ease with which it loses hydrogen chloride, and is converted into the compound $C_{10}H_8O_4$, thus:—

$$C_{10}H_9O_4Cl = C_{10}H_8O_4 + HCl.$$

This change takes place on heating at 150°, or on warming with alkalis or reducing with zinc-dust and acetic acid, and also on heating with methylamine in alcoholic solution in a sealed tube. In order to prevent this, the carboxyl group was protected by converting the chloro-acid into its methyl salt, $C_{10}H_8(CH_3)O_4Cl$. This methyl salt, when heated with methylamine in alcohol solution at 130° for six hours, and the product boiled with alcoholic potash, is almost quantitatively converted into oxyhydrastinine, thus:—



$$CH_2{<}\substack{O\\O}{>}C_6H_3{<}\substack{COOCH_3\\CH_2\cdot CH_2Cl} + 2NH_2\cdot CH_3 =$$

$$CH_3\cdot NH_2,HCl + CH_2{<}\substack{O\\O}{>}C_6H_3{<}\substack{COOCH_3\\CH_2\cdot CH_2\cdot NH\cdot CH_3} =$$

$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\begin{array}{l}CO\cdot NCH_3\\ \quad\quad\ |\\ CH_2\cdot CH_2\end{array} + CH_3\cdot OH.$$

Oxyhydrastinine.

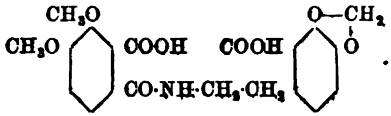
The substance thus obtained melts at 98°, and is identical with oxyhydrastinine, and the synthesis of this compound from ω-amidoethylpiperonylcarboxylic acid affords conclusive proof that the constitutional formulæ given above to this substance and its derivatives are correct.

An examination of these formulæ shows also that berberine is an isoquinoline and not a quinoline derivative, and the decomposition of berberilic acid into hempinic acid and ω-amidoethylpiperonylcarboxylic acid affords evidence that this alkaloïd must be closely related to papaverine, hydrastine, and narcotine (p. 1004).

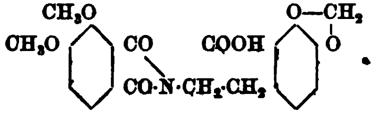
As berberine is an isoquinoline derivative, the statement of Bernheimer (*Gazzetta*, **13**, 342) that berberine, when fused with potash, yields quinoline cannot be correct; it is probable that the substance which he obtained was isoquinoline.

Constitution of Berberilic Acid and Anhydroberberilic Acid.

As berberilic acid is a bibasic acid, and as, on hydrolysis, it yields hempinic acid and ω-amidoethylpiperonylcarboxylic acid, its constitution must be represented by the formula

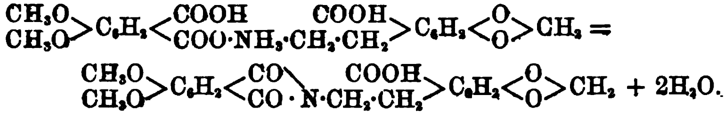


Anhydroberberilic acid is a monobasic acid, and is derived from berberilic acid by the elimination of one molecule of water; its formula is therefore



Additional proof of the correctness of these formulæ is afforded by the synthesis of anhydroberberilic acid.

This interesting synthesis is readily accomplished by heating the hemipinate of ω-amidoethylpiperonylcarboxylic acid, which is formed by evaporating mixed aqueous solutions of hempinic and ω-amidoethylpiperonylcarboxylic acids. This reaction is readily understood with the aid of the following equations:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COOH\qquad\qquad\quad COOH\\COO\cdot NH_3\cdot CH_2\cdot CH_2\end{matrix}>C_6H_3<\begin{matrix}O\\O\end{matrix}>CH_2 =$$

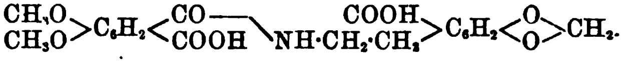
$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\diagdown\qquad COOH\\CO\cdot N\cdot CH_2\cdot CH_2\end{matrix}>C_6H_3<\begin{matrix}O\\O\end{matrix}>CH_2 + 2H_2O.$$

In Part I of this research (*loc. cit.*, pp. 78 and 84) two substances are described which have the same formula as berberilic acid.

One of these compounds melts at 140—141°, and is very closely related to berberilic acid, because, when heated to 180°, it, like berberilic acid, is quantitatively converted into anhydroberberilic acid; as, however, berberilic acid melts at about 180°, it would seem that the two acids are isomeric and not identical.

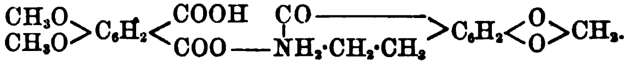
The melting point of berberilic acid is, however, lowered to an unusually marked degree by the least trace of impurity, and it is therefore necessary that further experimental data should be forthcoming, before the isomerism of the two acids can be considered as proved. It is, nevertheless, interesting to note that, theoretically, two substances of the formula $C_{20}H_{19}NO_9$ are possible, both of which on heating would be converted into the same anhydroberberilic acid; and there seems to be no reason why, by slightly altering the conditions of formation or hydrolysis, the acid isomeric with berberilic acid might not be formed.

The constitution of one of these isomeric acids would be represented by the formula given above for berberilic acid; the second acid would have the constitution represented by the formula



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}CO\text{——}\diagdown\\COOH\end{matrix}\;\begin{matrix}\\NH\cdot CH_2\cdot CH_2\end{matrix}\!\!\begin{matrix}COOH\\\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}O\\O\end{matrix}\!\!>CH_2.$$

The other substance of the formula $C_{20}H_{19}NO_8$ (*loc. cit.*, p. 84) melts at 178—179°, and is decomposed by warm dilute sodium carbonate into *hemipinic acid* and *ω-amidoethylpiperonylcarboxylic anhydride.* This substance must, therefore, be considered as the acid hemipinate of ω-amidoethylpiperonylcarboxylic anhydride, and its constitution is therefore:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}COOH\quad CO\text{————————}\\COO\text{——}NH_2\cdot CH_2\cdot CH_2\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}O\\O\end{matrix}\!\!>CH_2.$$

Examination of Berberal, $C_{20}H_{17}NO_7$.

The experiments on the constitution of berberal were rendered extremely difficult from the fact that this substance is only produced in very small quantity in the oxidation of berberine; about 10 grams of pure substance was obtained from 1 kilo. of berberine hydrochloride.

The preparation and some of the properties of berberal have already been given in Part I of this research (pp. 81, 82), and it was there stated that this substance, although insoluble in alkalis in the cold, was apparently converted into the potassium salt of an acid by dissolution in potassium hydrate. In following up this reaction, it was found that, when treated with alcoholic potash, berberal yields three substances, namely: ω-amidoethylpiperonylcarboxylic anhydride ($C_{10}H_9NO_3$); an acid $C_{10}H_{10}O_5$ (m. p. 121°), and a neutral substance $C_{20}H_{19}NO_8$ (m. p. 149°); these are formed according to the following equations:—

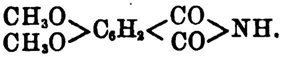
$$C_{20}H_{17}NO_7 + H_2O = C_{20}H_{19}NO_8,$$
$$C_{20}H_{19}NO_8 = C_{10}H_9NO_3 + C_{10}H_{10}O_5.$$

As the constitution of ω-amidoethylpiperonylcarboxylic anhydride has already been proved (p. 997), there is no further need of discussing this compound here.

The acid $C_{10}H_{10}O_5$ is a monobasic acid forming salts of the formula $C_{10}H_9O_5M'$; it shows the following behaviour with reagents: (*a*) When treated with hydrogen iodide in Zeisel's apparatus, results were obtained which proved that the acid contained two methoxyl groups. (*b*) Fusion with potash converts the acid into protocatechuic acid; but if caustic potash solution (sp. gr. 1·4) is employed, and the acid simply digested with this in a reflux apparatus, veratric acid (m. p. 177—178°) and apparently also formic acid are produced, thus:—

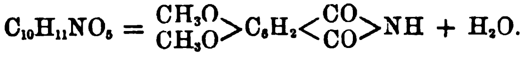
$$C_{10}H_{10}O_5 + 2KOH = (CH_3O)_2C_6H_3COOK + HCOOK + H_2O.$$

(*c*) When subjected to the action of hydroxylamine, an oxime, $C_{10}H_{11}NO_5$, is produced. This melts at about 124°, but at once becomes solid again, and then does not again melt until the temperature is raised to 213°. Further experiments showed that this behaviour was due to the formation of hemipinimide:—



$$\begin{array}{l}CH_3O\\CH_3O\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}CO\\CO\end{array}\!\!>NH.$$

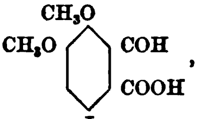
This decomposition is represented by the equation



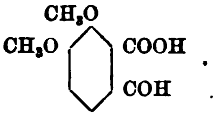
$$C_{10}H_{11}NO_5 = \begin{array}{l}CH_3O\\CH_3O\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}CO\\CO\end{array}\!\!>NH + H_2O.$$

(*d*) It is readily reduced by sodium amalgam, being converted into an acid, which when precipitated from its alkaline solution by the addition of mineral acids and recrystallised from water, loses 1 mol. of water, with formation of pseudomeconine, $\begin{array}{l}CH_3O\\CH_3O\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}CH_2\\CO\end{array}\!\!>O$.

These experiments prove conclusively that the acid $C_{10}H_{10}O_5$ has the constitution represented by the formula I, and it thus bears a very close relationship to *opianic acid*, II—



I.



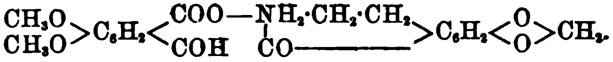
II.

This relationship is brought out in a most interesting way by a parallel study of the reactions of the two substances; for instance, both are monobasic acids; both contain two methoxyl groups in the ortho-position; both, on reduction, yield meconines, and with hydroxylamine both yield oximes, which, when gently warmed, are converted into hemipinide. The acid $C_{10}H_{10}O_6$ may, therefore, be called *pseudopianic acid.*

The hydrolysis of berberal by means of dilute sulphuric acid was next studied, with the result that exactly similar decomposition products were formed in this case as in the hydrolysis by means of alcoholic potash, namely, the anhydride $C_{10}H_9NO_3$, pseudopianic acid, and the neutral substance $C_{20}H_{19}NO_6$.

Owing to the difficulty of obtaining any quantity of berberal, and the inadvisability of using up, for purely qualitative experiments, the small stock of this substance available, further information bearing on the constitution of this compound had to be in the first place obtained indirectly.

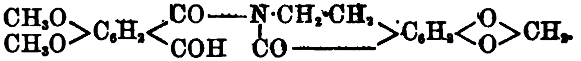
For this purpose a number of experiments on the action of opianic acid (from narcotine) on the anhydride $C_{10}H_9NO_3$ were instituted and it was found that if these two compounds, in molecular proportions, are well mixed and dissolved in boiling water, a new substance, $C_{20}H_{19}NO_8$, crystallises out on cooling; this in its reactions shows very great similarity to the isomeric substance obtained from berberal, with which, however, it is not identical. The new compound is obviously the opianic salt of the anhydride $C_{10}H_9NO_3$, and its constitution is therefore represented by the formula



$$\genfrac{}{}{0pt}{}{\mathrm{CH_3O}}{\mathrm{CH_3O}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{COO-NH_2\cdot CH_2\cdot CH_2}}{\mathrm{COH\quad CO}\text{————}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}>\mathrm{CH_2}.$$

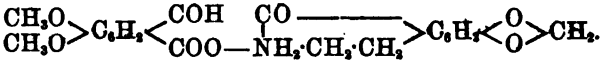
The most interesting property of this salt is that, when heated at 200°, it loses the elements of a molecule of water, and is converted into a compound $C_{20}H_{17}NO_7$ (m. p. 185°), which is isomeric with, and bears the strongest resemblance to berberal, for which reason I propose to name it *isoberberal*.

The constitution of this compound is represented by the formula



$$\genfrac{}{}{0pt}{}{\mathrm{CH_3O}}{\mathrm{CH_3O}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{CO-N\cdot CH_2\cdot CH_2}}{\mathrm{COH\quad CO}\text{————}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}>\mathrm{CH_2}.$$

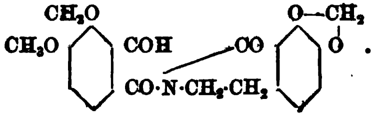
These experiments were next repeated with pseudopianic acid instead of opianic acid, with the result that exactly similar compounds were obtained. Pseudopianic acid and the anhydride $C_{10}H_9NO_3$ combine readily in aqueous solution with formation of the pseudopianic salt of the anhydride $C_{10}H_9NO_3$. This substance is identical with the compound $C_{20}H_{19}NO_8$, which is obtained by the action of alkalis on berberal. It is isomeric with the substance obtained by the action of opianic acid on the anhydride $C_{10}H_9NO_3$, and has the constitution represented by the formula



$$\genfrac{}{}{0pt}{}{\mathrm{CH_3O}}{\mathrm{CH_3O}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{COH\quad CO}\text{————}}{\mathrm{COO-NH_2\cdot CH_2\cdot CH_2}}>\mathrm{C_6H_2}<\genfrac{}{}{0pt}{}{\mathrm{O}}{\mathrm{O}}>\mathrm{CH_2}.$$

The relationship between these two substances is at once apparent from a comparison of their constitutional formulæ.

Just as the opianic salt of the anhydride $C_{10}H_9NO_3$, on heating at 180—200°, yields *isoberberal*, so this corresponding pseudopianate, under the same conditions, is converted almost quantitatively into berberal. *Berberal* has therefore the following constitutional formula:—



The synthesis of berberal may be still more conveniently accomplished by heating an intimate mixture of pseudopianic acid and the anhydride $C_{10}H_9NO_3$, in molecular proportion, at 200° for a few minutes. The reaction which takes place under these circumstances is the following:—

$$C_{10}H_{10}O_5 + C_{10}H_9NO_3 = C_{20}H_{17}NO_7 + H_2O.$$

There is a possibility of synthesising berberine from berberal, and if this were to succeed, a most interesting isomeric alkaloïd could be obtained from isoberberal. Experiments on this point are in progress.

Oxyberberine, $C_{20}H_{17}NO_5$.—This substance, which is formed only in very small quantities by the oxidation of berberine under the conditions described in this paper, is insoluble in alkalis, but combines with strong acids, forming salts; its basic properties are, however, very much less marked than those of berberine itself.

Oxyberberine is a tertiary base, incapable of forming an acetyl compound. It does not appear to combine with phenylhydrazine; it is not decomposed on boiling with alcoholic potash or on heating with alcoholic ammonia at 150°.

Dioxyberberine, $C_{20}H_{17}NO_6$.—This extremely interesting substance has scarcely any basic properties, but it dissolves in warm alcoholic potash, forming a deep-red solution; this, on cooling, deposits a beautiful, crystalline potassium salt, $C_{20}H_{18}NO_7K$, which is decomposed by acids with regeneration of dioxyberberine. In contact with oxygen or air, the solution of the potassium salt gradually loses its red colour, and in the course of a few days becomes almost colourless; on the addition of acids it then deposits a white precipitate of berberilic acid. This remarkable reaction may be represented by the equation

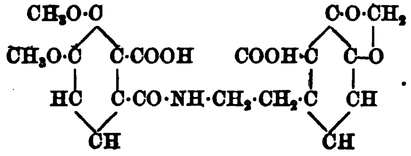
$$C_{20}H_{18}NO_7K + KOH + O_2 = C_{20}H_{17}NO_9K_2 + H_2O.$$

Further experiments will, it is hoped, throw some light on this very peculiar reaction.

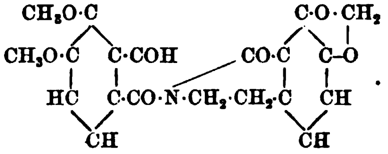
Constitution of Berberine.—Although not conclusively proved by the above experiments, the constitution of berberine may be deduced with a considerable amount of certainty from the results obtained in the study of the constitution of berberilic acid and of berberal.

These two substances have the following constitutional formulæ:—

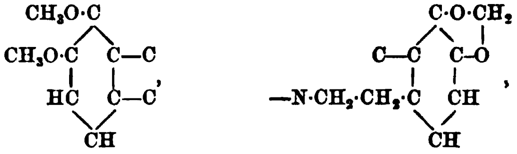
Berberilic acid,



Berberal,



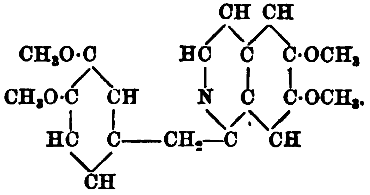
From an examination of these formulæ, it is readily seen that berberine, $C_{20}H_{17}NO_4$, must contain the following groups of atoms:—



and as these already contain C_{20}, H_{16}, N, O_4, it follows that, in assigning a constitutional formula to berberine, these two parts must be united with the addition of one atom of hydrogen only.

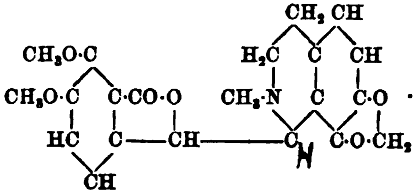
As the decomposition products of berberine are in many respects very similar to those obtained from papaverine, hydrastine, and narcotine, it is reasonable to suppose that these four alkaloïds are all very closely related in constitution. The following formulæ are generally accepted as representing the constitution of papaverine, hydrastine, and narcotine:—

Papaverine (Goldschmiedt, *Monatsh.*, **6**, 667),

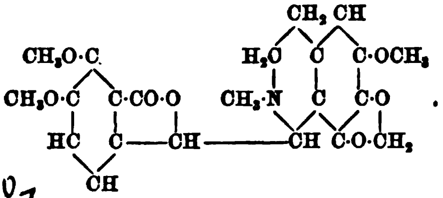


$C_{20}H_{21}NO_4$

Hydrastine (Freund and Rosenberg, *Ber.*, **23**, 414),

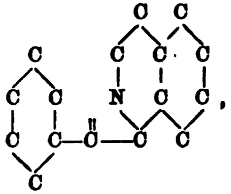


Narcotine (Roser, *Annalen*, **254**, 357),



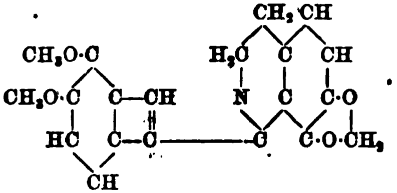
$C_{22}H_{23}NO_7$

These alkaloïds are all built upon the common foundation



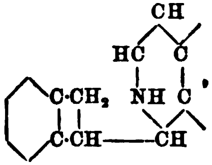
and a careful study of the properties of berberine and its derivatives leaves scarcely any doubt that this group of atoms or one very similar occurs also in berberine.

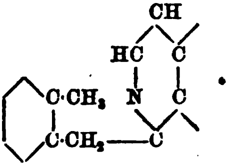
With this point in view, the simplest formula for berberine would be



$C_{20}H_{17}NO_4$

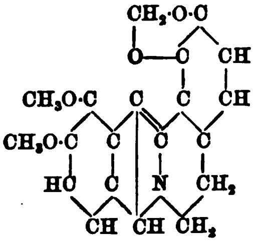
Berberine, when reduced, yields *tetrahydroberberine*, $C_{20}H_{21}NO_4$. This substance is a tertiary base. On treatment with oxidising agents (bromine, iodine, nitric acid, &c.), it is very readily reconverted into berberine; its constitution cannot therefore be derived from the above formula, as this, on reduction, would yield a compound which would contain one of the following two groups:—

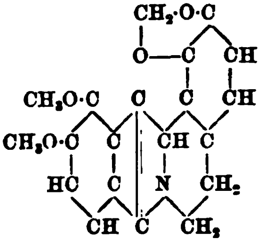




A substance containing the former would be a secondary base, and a compound containing the latter would obviously not be reconverted into the alkaloïd on treatment with such oxidising agents as iodine.

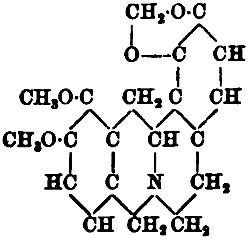
There are, however, two formulæ, closely allied to the one given above, and built upon a very similar foundation, which account, in a satisfactory manner, for all the known reactions of berberine, namely :—

I.  ,

II.  ,

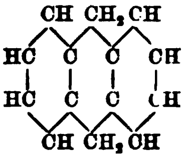
and, of these, formula I would seem to be the more plausible.

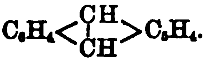
Both of these formulæ yield, on reduction, the same tetrahydroberberine :—

 .

This formula accounts at once for the ready way in which tetrahydroberberine is reconverted into berberine on oxidation, as is apparent from the following considerations :—

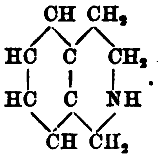
In the first place, this formula contains a group of atoms very similar to that contained in hydranthracene,

 ,

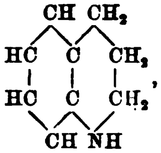
and this substance, on oxidation, is converted with the greatest ease into anthracene,  $C_6H_4<\begin{matrix}CH\\|\\CH\end{matrix}>C_6H_4$.

This point is still more clearly brought out from the comparison of the above formula for tetrahydroberberine with that of dihydroacridine,* $C_6H_4{<}\begin{smallmatrix}CH_2\\ NH\end{smallmatrix}{>}C_6H_4$, a substance which, when treated even with such feeble oxidising agents as alcoholic nitrate of silver, loses two atoms of hydrogen with formation of acridine, $C_6H_4{<}\begin{smallmatrix}CH\\ |\\ N-\end{smallmatrix}{>}C_6H_4$. From these considerations, it would appear at first sight as though tetrahydroberberine, $C_{20}H_{21}NO_4$, should, on oxidation, lose only two atoms of hydrogen with formation of a substance of the formula $C_{20}H_{19}NO_4$.

Tetrahydroberberine is, however, a derivative of tetrahydroisoquinoline,



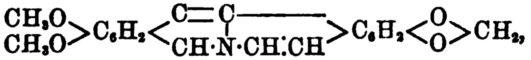
This substance has lately been prepared by Hoogewerff and Van Dorp (*Recueil des travaux chimiques des Pays-Bas*, **5**, 310), and has been found to be readily oxidised even by nitrate of silver, but the products of the oxidation have not yet been studied. On the other hand, tetrahydroquinoline,



which is very closely related to tetrahydroisoquinoline, is readily oxidised by bromine or dilute chromic acid solution to quinoline and its derivatives.

It is interesting to note that berberine itself contains a dihydroisoquinoline group, and the presence of this group accounts for the fact that the alkaloïd reduces nitrate of silver, and is so readily attacked by oxidising agents.

It is hoped that further experiments, which are in progress, will succeed in removing the two hydrogen atoms; and that in this way the mother substance of berberine, that is,



$$\begin{matrix}CH_3O\\ CH_3O\end{matrix}{>}C_6H_2{<}\begin{matrix}C{=}C\text{————}\\ CH{\cdot}\overset{|}{N}{\cdot}CH{:}CH\end{matrix}{>}C_6H_2{<}\begin{matrix}O\\ O\end{matrix}{>}CH_2,$$

may be obtained.

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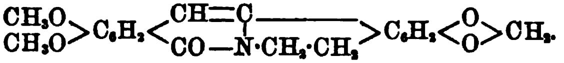
* See also dihydrophenylacridine (Bernthsen, *Annalen*, **224**, 25), and methylhydrophenylacridine (Bernthsen, Bender, *Ber.*, 16, 1815).

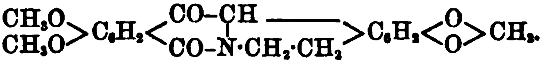
Assuming formula I (p. 1006) to represent the constitution of berberine, the constitution of oxyberberine and dioxyberberine is readily understood from the following formulæ:—

Oxyberberine,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{array}{l}CH{=}C\text{————————}\\ \qquad\;\;|\\ CO-N\cdot CH_2\cdot CH_2\end{array}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2.$$

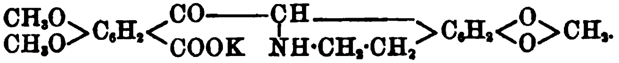
Dioxyberberine,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{array}{l}CO-CH\text{ ————}\\ \qquad\;\;|\\ CO-N\cdot CH_2\cdot CH_2\end{array}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2.$$

These formulæ explain the general character and reactions of these substances, and give a clear insight into the processes which take place in the production of these compounds from berberine, and in the subsequent splitting up of the central oxidised ring with formation of berberal and anhydroberberilic acid.

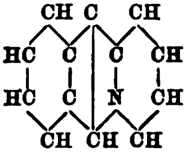
The dioxyberberine formula also explains the fact that this substance, on treatment with alcoholic potash, yields a potassium salt of the formula $C_{20}H_{18}NO_7K$; this would have the constitution



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{array}{l}CO\text{———}CH\text{————}\\ \qquad\qquad\;\;|\\ COOK\quad NH\cdot CH_2\cdot CH_2\end{array}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2.$$

It is, however, difficult to account for the conversion of this salt into a salt of berberilic acid by the absorption of oxygen in alkaline solution.

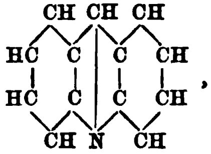
With the introduction of each oxygen atom into the molecule of berberine, the basic nature of the substance, and at the same time the intensity of its colour, decreases, until, as soon as the central ring is split, as in the case of berberal and anhydroberberilic acid, the derivatives become colourless, and show no appreciable basic properties. On the other hand, the methoxy-groups and the methylenedioxy-group appear to have little influence on the tinctorial property of berberine, because other alkaloïds, such as narcotine and hydrastine, which are somewhat similarly constituted, and contain the same number, or even more, of such groups, are colourless. The group of atoms which appears to impart to berberine its intense yellow colour and tinctorial properties is the strongly basic group



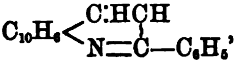
,

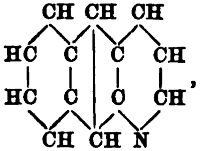
which is absent in the colourless alkaloïds papaverine, hydrastine, and narcotine. This group does not appear to have yet been investigated; but there are, on the other hand, a number of substances which contain groups of atoms very closely allied to this, and it is interesting to note that the salts of such substances, like those of berberine, are intensely yellow. The following instances, taken from a large number, will illustrate this point.

The whole series of *acridine* derivatives which contain the group



although sometimes colourless themselves, invariably yield intensely yellow salts.

α-Phenyl-α-naphthaquinoline,  $C_{10}H_6<\begin{matrix}C{:}HCH\\ N{=}C{-}C_6H_5\end{matrix}$, which contains the very similarly constituted group,

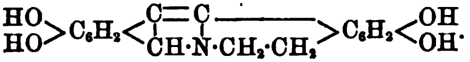


is yellow, and its salts are also intensely yellow. These instances might be multiplied to a considerable extent. It appears therefore that the formula proposed for berberine is in harmony with the fact that the alkaloïd is so intensely yellow. In Part I of this research (*loc. cit.*, p. 88), a substance is described, which results from the action of hydriodic acid on berberine, and which was termed berberoline. This compound (of which the sulphate was analysed) was then thought to have the composition $C_{18}H_{11}NO_2(OH)_2$. It is, however, evident that this formula cannot be correct, as it is obviously produced from berberine by the elimination of the methylene and the methyl groups, thus:—

$$C_{20}H_{17}NO_4 + 4HI = C_{17}H_9N(OH)_4 + CH_2I_2 + 2CH_3I.$$

The analysis already given agrees well with the new formula.

The constitution of *berberoline* is represented by the formula



$$\begin{matrix}HO\\HO\end{matrix}>C_6H_2<\begin{matrix}C=C\text{————}\\ CH\cdot N\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}OH\\OH\end{matrix}.$$

In the experimental part of this paper, a number of substances are described, some of which afford additional evidence as to the constitution of berberine, others, at first sight, appear to have little connection with this problem; but it must be borne in mind that these new compounds were prepared and examined at a time when very little was known as to the constitution of the alkaloïd, and when their examination appeared likely to give important clues to the nature of the various complicated substances which were obtained from time to time.

I cannot conclude this part of the paper without expressing my thanks to Mr. Bertram Prentice for the very valuable assistance which he rendered, especially in the preparation of the large amount of material necessary for these experiments.

Oxidation of Berberine with Potassium Permanganate.

In continuing the investigation of the action of potassium permanganate on berberine, special care was taken that the berberine hydrochloride employed was pure, so that no doubt should exist that all the substances subsequently obtained were actually derived from berberine itself, and not from a small quantity of some other alkaloïd admixed therewith.

Commercial berberine hydrochloride, obtained from Merck, in Darmstadt, was first recrystallised from water, then dissolved in water, and the solution boiled with a small quantity of pure precipitated calcium carbonate for a few minutes; the liquid, originally of a yellow colour, is rendered distinctly brownish by this treatment, but the filtered solution, on cooling, deposits long, light brown needles of almost pure berberine hydrochloride, and these, after well washing and drying on a porous plate for some days at the ordinary temperature, gave the following numbers on analysis:—

I. 0·1484 gram substance gave 0·0806 gram H_2O and 0·2950 gram CO_2.

0·5249 gram substance heated with nitrate of silver and nitric acid in a sealed tube gave 0·1592 gram AgCl.

0·3354 gram substance gave 9·5 c.c. N.; $t = 16°$; bar. = 740 mm.

II. 0·1956 gram substance gave 0·1058 gram H_2O and 0·3884 gram CO_2.

	Theory. $C_{20}H_{17}NO_4HCl + 4H_2O$.	Found. I.	Found. II.
C......	54·13 per cent.	54·21	54·15 per cent.
H.....	5·86 „	6·03	6·03 „
Cl.....	7·98 „	7·62	— „
N.....	3·16 „	3·21	— „

Although the crystals obtained by this treatment are slightly brownish, this method of purification was almost always employed.

Recrystallisation first from dilute alcohol, and then from very dilute hydrochloric acid, entirely removes the brownish tinge, and the crystals have then a fine yellow colour and satiny lustre. In investigating the products formed by the oxidation of berberine by potassium permanganate, the following were the quantities usually employed:—

Berberine hydrochloride	7 grams.
Potassium permanganate	9 „
Dry potassium carbonate.........	1 „

In those cases, however, where an increased yield of some one of the oxidation products was desired, these quantities were varied, proportions more favourable to the formation of that particular product being employed, as will be mentioned in the description of the individual substances. The berberine hydrochloride was dissolved in about half a litre of water, at a temperature of about 70°, the potassium carbonate added, and then the strong hot solution of the permanganate, in half a litre of water, run in moderately rapidly, either drop by drop, or in a very fine stream from a tap funnel. The product from a large number of such operations was well cooled, treated with sulphurous anhydride (as explained in Part I, p. 77), and thus separated into a yellow, flocculent *precipitate* and a yellowish-coloured *solution*. The treatment of the *precipitate* was as follows:—The yellow, amorphous mass was thoroughly washed by grinding up with water, filtering through cloth, and squeezing; this operation being repeated at least three times, and the washings always added to the original *solution*. The *precipitate*, which, after drying on a porous plate, amounts to about 40 per cent. of the berberine hydrochloride used, was treated with dilute sodium carbonate solution, substantially in the same way as previously described (Part I, pp. 77–78), and thus separated into two portions:—

I. *Soluble in Sodium Carbonate.*—This contains the acid $C_{20}H_{19}NO_9$ (α-berberilic acid), and a certain amount of the substance $C_{20}H_{17}NO_8$ (anhydroberberilic acid). Both of these compounds have been already described (Part I, pp. 78–80).

II. *Insoluble in Sodium Carbonate.*—This portion is further resolved by boiling with acetic acid into *anhydroberberilic* acid, $C_{20}H_{17}NO_8$ (see p. 1037); *berberal*, $C_{20}H_{17}NO_7$ (see p. 1062); and berberine hydrogen sulphite, $C_{20}H_{17}NO_4,H_2SO_3$ (see p. 1097).

The *solution*, which in bulk frequently amounted to 150—200 litres, was rapidly evaporated in large, flat, enamelled iron pans, until its volume had been reduced by about one half. During the evaporation a quantity of a yellow, flocculent substance separated, consisting for the most part of inorganic salts, but containing also, as examination showed, a considerable quantity of organic matter. This precipitate was collected on cloth bags, washed with water, transferred to a large evaporating basin, and gently warmed with a considerable bulk of 5 per cent. hydrochloric acid; quantities of sulphurous anhydride were evolved, and the greater part of the substance went into solution. The insoluble matter was collected, washed with water, and treated with very dilute hydrochloric acid, until the resulting yellow mass contained only traces of inorganic matter. This crude substance contains, besides varying quantities of anhydroberberilic acid, two new compounds, $C_{20}H_{17}NO_5$ (oxyberberine, p. 1085) and $C_{20}H_{17}NO_6$ (dioxyberberine, p. 1087); the methods of separation of these are given on pp. 1083–4.

The liquors from which this insoluble matter had been separated were again concentrated to half their bulk, allowed to cool, the inorganic salts which separated discarded, and the evaporation carefully continued until slight decomposition took place, as shown by rapid discoloration accompanied by empyreumatic odours. The liquor was transferred to large bottles, and extracted at least 20 times with ether, the separation of the two liquids being effected by syphoning off the aqueous layer. The colourless ethereal solution, which has a strong blue fluorescence, was evaporated in a large flask, and the semi-solid residue (about 35 grams from each kilo. of berberine hydrochloride used), which contains the substance $C_{20}H_{19}NO_9$ (see Part I, p. 84), hemipinic acid, and other products was treated as follows:—About ¾ litre of hot water was added, the whole heated on a sand-bath for five minutes, with sufficient sodium carbonate to make the solution decidedly alkaline, and the liquid rapidly filtered through a jacketed funnel. A small quantity of a dirty grey, insoluble substance (see p. 1094) which contained hemipinic anhydride was left on the paper.

The alkaline solution on cooling deposited a considerable quantity (about 13—14 grams) of beautiful, leafy crystals of a new substance, $C_{10}H_9NO_3$ (ω-amidoethylpiperonylcarboxylic anhydride), an exhaustive examination of which is given on p. 1013. The filtrate from these crystals was concentrated, allowed to stand 48 hours, so as to completely deposit any further quantities of the anhydride, $C_{10}H_9NO_3$, filtered, acidified with dilute hydrochloric acid, and gently warmed. A small quantity of a greyish substance which contained a new acid, $C_{20}H_{15}NO_8$ (berilic acid), remained undissolved, and was removed by filtration (see p. 1091).

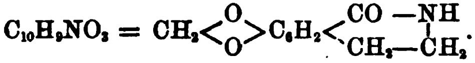
The filtrate from this was repeatedly extracted with ether, and the ethereal solution evaporated, when a quantity of a yellowish semi-solid mass remained. This contains hemipinic acid, $C_{10}H_{10}O_6$, and hydrastic acid, $C_9H_6O_6$; the method of separation and purification of these acids is given on p. 1095.

The original concentrated solution which had been extracted with ether contains, besides the bulk of the inorganic salts, large quantities of organic matter, which appears to consist for the most part of hemipinic acid, together with varying quantities of the anhydride, $C_{10}H_9NO_3$, mentioned above.

The examination of these liquors is given on p. 1105. A long series of operations such as those involved in the separation of the numerous oxidation products of berberine is difficult to follow from mere description, and I have thought that it might facilitate reference if the methods employed were summarised in tabular form (p. 1014).

The following pages contain a detailed examination of the substances obtained from berberine by oxidation, as explained in the preceding pages.

ω-Amidoethylpiperonylcarboxylic Anhydride,



$$C_{10}H_9NO_3 = CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}CO-NH\\CH_2-CH_2\end{matrix}.$$

The crude product, the preparation of which is given on p. 1012, is readily purified by recrystallisation from boiling water, and is thus obtained in beautiful, colourless plates, which, after drying at 100°, gave the following results on analysis:—

I. 0·1196 gram substance gave 0·0554 gram H_2O and 0·2753 gram CO_2.

0·1476 gram substance gave 9·1 c.c. N; $t = 17$; bar. = 740 mm.

II. 0·1370 gram substance gave 0·0600 gram H_2O and 0·3143 gram CO_2.

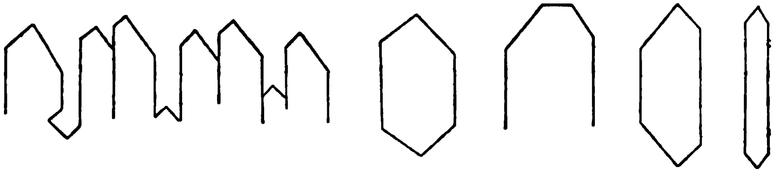
	Theory. $C_{10}H_9NO_3$.	Found. I.	Found. II.	
C	62·82 per cent.	62·77	62·56	per cent.
H	4·71 „	5·15	4·79	„
N.......	7·33 „	7·23	—	„

This beautiful substance melts at 181—182°; when rapidly heated in small quantities in a test tube, it distils with only slight decomposition, and the oily distillate, on cooling, solidifies to a mass of colourless plates. It is very sparingly soluble in cold, but readily in hot water, the hot solution, on cooling, depositing beautiful, very characteristically shaped crystals, often grouped together in masses

Berberine Hydrochloride is Oxidised with Potassium Permanganate, the Product treated with Sulphurous Anhydride, (see p. 1011) and Filtered.

<table>
<tr><td colspan="4"><i>Yellow precipitate</i> treated with warm dilute sodium carbonate solution and filtered.</td><td colspan="6"><i>Yellow filtrate</i> evaporated to half its bulk and filtered.</td></tr>
<tr><td colspan="3"><i>Residue</i> boiled with acetic acid and filtered hot.</td><td rowspan="5"><i>Solution</i> contains Berberilic acid, $C_{20}H_{19}NO_9$, and some Anhydroberberilic acid, $C_{20}H_{17}NO_8$ (p. 1087).</td><td rowspan="5"><i>Precipitate contains</i> Oxyberberine, $C_{20}H_{17}NO_5$ (p. 1085). Dioxyberberine, $C_{20}H_{17}NO_6$ (p. 1087). Anhydroberberilic acid, $C_{20}H_{17}NO_8$ (p. 1087).</td><td colspan="5"><i>Solution</i> evaporated to half its bulk and extracted 20 times with ether.</td></tr>
<tr><td rowspan="4"><i>Residue</i> contains Berberine hydrogen sulphite, $C_{20}H_{17}NO_4H_2SO_3$ (p. 1097).</td><td colspan="2"><i>Solution</i> on cooling deposits crystals which are separated by filtration.</td><td colspan="4"><i>Ethereal solution</i> evaporated, residue boiled with dilute sodium carbonate solution and filtered hot.</td><td rowspan="4"><i>Aqueous solution</i> contains Hemipinic acid, $C_{10}H_{10}O_6$, ω-Amido-ethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_3$, and inorganic salts (p. 1105).</td></tr>
<tr><td rowspan="3"><i>Residue</i> consists of Anhydroberberilic acid, $C_{20}H_{17}NO_8$ (p. 1087).</td><td rowspan="3"><i>Solution</i> contains Berberal, $C_{20}H_{17}NO_7$ (p. 1062).</td><td rowspan="3"><i>Residue</i> contains Hemipinic anhydride, $C_{10}H_8O_5$ (p. 1094).</td><td colspan="3"><i>Solution</i> allowed to cool and filter.</td></tr>
<tr><td rowspan="2"><i>Crystals</i> of ω-Amido-ethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_3$ (p. 1013).</td><td colspan="2"><i>Solution</i> acidified with hydrochloric acid and filtered.</td></tr>
<tr><td><i>Residue</i> contains Berilic acid, $C_{20}H_{15}NO_8$ (p. 1091).</td><td><i>Solution</i> contains Hydrastic acid, $C_9H_6O_6$, and Hemipinic acid, $C_{10}H_{10}O_6$ (p. 1096).</td></tr>
</table>

very much resembling the teeth of a saw. These, when examined under the microscope, present the following appearance:—



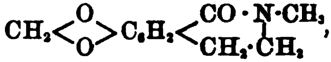
It is very readily soluble in warm methyl alcohol; the warm solution, on slowly cooling, or, better still, on spontaneous evaporation, deposits well-formed, tabular crystals, which have a beautiful lustre. When examined under the microscope, these are seen to have forms almost exactly similar to those drawn above, the only difference being that the crystals from methyl alcohol were single examples and very well shaped, twins being almost entirely absent.

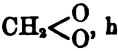
The anhydride $C_{10}H_9NO_3$ is also readily soluble in ethyl alcohol and in boiling benzene, xylene, or toluene, extremely soluble in chloroform and acetic acid, sparingly in ether, and almost insoluble in light petroleum. It crystallises from hot benzene in long, flat, ill-shaped plates. Its hot dilute aqueous solution gives no precipitate with mercuric chloride, but, on cooling, beautiful, colourless needles of a double compound separate. These are readily soluble in boiling water.

With a solution of phosphomolybdic acid, an aqueous solution of the anhydride $C_{10}H_9NO_3$, acidified with hydrochloric acid, even when very dilute, gives a yellowish-white precipitate, which dissolves appreciably in boiling water.

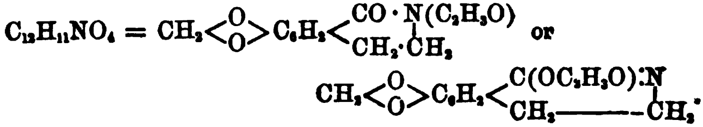
The anhydride $C_{10}H_9NO_3$ is insoluble in caustic potash solution, even on boiling; it dissolves readily in strong acids, forming salts, which, however, are very unstable, and could not be obtained in a state fit for analysis. From hot dilute acids, the substance crystallises unchanged.

Fusion of the Anhydride $C_{10}H_9NO_3$ *with Potash.*—Although it is not dissolved on boiling with strong solutions of potassium hydrate, the compound is readily decomposed by fusion with potash. It first of all melts to an oil, ammoniacal vapours are given off, and in a short time a clear, slightly brownish melt is formed. This is soluble in water, producing a purplish solution, which changes colour in the way so characteristic of a protocatechuic acid melt, and on acidifying and extracting with ether, a semi-solid mass is obtained, which shows the ferric chloride and other reactions of catechol or protocatechuic acid, and probably consists of a mixture of both these substances.

Attempts to obtain a Methyl Derivative of the Anhydride $C_{10}H_9NO_3$.—As already mentioned in the Introduction, the substance $C_{10}H_9NO_3$ is closely related to oxyhydrastinine,  $CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{CO\cdot N\cdot CH_3}{CH_2\cdot CH_2}$, and numerous experiments were made with the object of converting the former into the latter by treatment with methyl iodide under very varied conditions. The following is a short account of these experiments:—

1. The finely powdered substance $C_{10}H_9NO_3$ was heated for four hours with a large excess of methyl iodide in a flask connected with a reflux apparatus. The methyl iodide was then distilled off, and the residue recrystallised from water. The crystals obtained melted at 182—183°, and consisted of unchanged substance.
2. The substance $C_{10}H_9NO_3$ was dissolved in alcohol and heated at 100° with excess of methyl iodide in a sealed tube for five hours. No action took place.
3. 2 grams of the substance $C_{10}H_9NO_3$ was dissolved in a solution of 0·6 gram of caustic potash in pure methyl alcohol, 2 grams of methyl iodide added, and the mixture heated in a sealed tube at 100° for five hours. On cooling, a quantity of the unchanged substance separated, and from the solution the remainder was readily obtained by distilling off the alcohol and adding water.
4. 1·2 grams of the substance $C_{10}H_9NO_3$ was dissolved in a solution of sodium methoxide (containing 2 grams of sodium) and heated with 8 grams of methyl iodide at 140° for five hours. The clear solution was evaporated, the residue dissolved in a little cold water, acidified, and extracted with ether. A yellowish oil, readily soluble in water, was obtained; the solution gave with ferric chloride a dark-green coloration, showing that decomposition of the methylenedioxy-group,  $CH_2<\genfrac{}{}{0pt}{}{O}{O}$, had taken place (see footnote, p. 996).

Acetyl-ω-amidoethylpiperonylcarboxylic Anhydride,



$$C_{13}H_{11}NO_4 = CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{CO\cdot N(C_2H_3O)}{CH_2\cdot CH_2} \text{ or }$$

$$CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{C(OC_2H_3O){:}N}{CH_2\text{———}CH_2}.$$

In order to prepare this substance, the pure anhydride $C_{10}H_9NO_3$ was dissolved in acetic anhydride and the solution boiled for four hours in a flask connected with a reflux apparatus. The excess of acetic anhydride and acetic acid was distilled off until only a small quantity of liquid remained, and this on cooling almost completely solidified to a cake of crystals. These were collected, well drained on a porous plate, dried at 110°, and analysed, with the following result:—

0·1578 gram substance gave 0·0692 gram H_2O and 0·3590 gram CO_2.

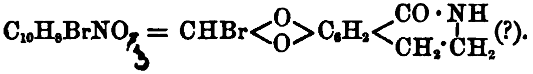
	Theory. $C_{12}H_{11}NO_4$.	Found.
C	61·80 per cent.	62·04 per cent.
H	4·72 „	4·87 „

This acetyl derivative crystallises from acetic anhydride in colourless needles which melt at 128—130°. It is readily hydrolysed on boiling with acids or alkalis, and, in order to further prove its constitution, a weighed quantity was hydrolysed and the amount of acetic acid produced estimated.

1·1086 gram substance was boiled with 30 per cent. sulphuric acid until completely dissolved, and the liquid distilled, with the addition of water when necessary, until the distillate no longer showed acid reaction.

The distillate required for complete neutralisation 49·7 c.c. of standard potassium hydrate solution (1 c.c. of which = 0 00597 c.c. acetic acid). 0·2967 gram of acetic acid was therefore produced, = 26·76 per cent. $C_{12}H_{11}NO_4$ on hydrolysis should yield 25·75 per cent. of acetic acid.

Amidoethylbromopiperonylcarboxylic Anhydride,



$$C_{10}H_8BrNO_3 = CHBr{<}{}^{O}_{O}{>}C_6H_2{<}\begin{matrix}CO\cdot NH\\ |\\ CH_2\cdot CH_2\end{matrix}\ (?).$$

When treated with bromine, the anhydride $C_{10}H_9NO_3$ is readily attacked, one atom of bromine replacing one atom of hydrogen in the molecule, forming a compound of the formula $C_{10}H_8BrNO_3$. As the bromine atom in this compound is very readily removed by nitric acid and silver nitrate, it can scarcely be situated in the benzene ring, and it is probable that the substitution takes place in the methylene dioxy-group, and that the compound has the constitutional formula given to it above.

The compound $C_{10}H_8BrNO_3$ is readily prepared by exposing finely-powdered ω-amidoethylpiperonylcarboxylic anhydride, $C_{10}H_9NO_3$, (p. 1013) to the action of a large excess of bromine vapour, under a bell jar, in direct sunlight. After standing for two days, the original white powder has become converted into a dark-brown syrup; this, on exposure to a current of air, loses its excess of bromine, yielding an ochre-coloured mass. This crude substance is best purified by repeated recrystallisation from boiling amyl alcohol, from which it is deposited on cooling in light-yellow, feathery crystals; these, after washing first with amyl alcohol and then with methyl alcohol and drying at 105°, gave the following results on analysis:—

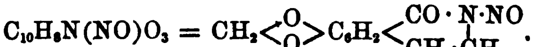
0·2003 gram substance gave 0·0564 gram H_2O and 0·3294 gram CO_2.

0·2240 gram substance, heated with nitric acid and silver nitrate in a sealed tube at 130—140°, gave 0·1543 gram AgBr.

	Theory. $C_{10}H_8BrNO_3$.	Found.
C	44·44 per cent.	44·85 per cent.
H........	2·97 ,,	3·12 ,,
Br........	29·63 ,,	29·38 ,,

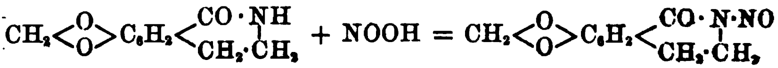
The bromo-derivative melts at 238—240°. It is readily soluble in chloroform, in boiling acetic acid, and in amyl alcohol; moderately soluble in hot xylene and alcohol, sparingly in carbon bisulphide, benzene, and light petroleum. It crystallises from amyl alcohol or xylene in slender, pale-yellow needles. It is readily decomposed by nitric acid and silver nitrate at ordinary temperatures, with separation of silver bromide.

Nitrosoamidoethylpiperonylcarboxylic Anhydride,



$$C_{10}H_8N(NO)O_3 = CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\cdot N\cdot NO\\ \vert\\ CH_2\cdot CH_2}.$$

When treated with nitrous acid, the anhydride $C_{10}H_9NO_3$ (p. 1013) behaves as a secondary base, yielding a well-defined and very characteristic nitroso-derivative according to the equation



$$CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\cdot NH\\ \vert\\ CH_2\cdot CH_2} + NOOH = CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\cdot N\cdot NO\\ \vert\\ CH_2\cdot CH_2} + H_2O.$$

In preparing this substance the following quantities were found to give good results:—

$C_{10}H_9NO_3$ (finely powdered)	3 grams.
Hydrochloric acid (sp. gr. 1·1)	100 c.c.
Water	75 ,,
Solution of sodium nitrite containing 10 grams $NaNO_2$ in 100 c.c. water..........	15 ,,

The substance $C_{10}H_9NO_3$ is first dissolved in the hydrochloric acid (this being readily accomplished by warming gently on a water-bath), the water is then added, the solution rapidly cooled to 20°, and lastly, the nitrite solution is run in, the flask being well cooled during the operation. The first few drops of the nitrite cause the solution to acquire a deep reddish-brown colour; this, however, soon disappears, and is succeeded by the separation of a yellow, amorphous precipitate, which ultimately causes the liquid to become quite thick. The whole operation must be quickly performed, otherwise the substance $C_{10}H_9NO_3$ is apt to crystallise out of the hydrochloric acid, and thus escape the action of the nitrous acid.

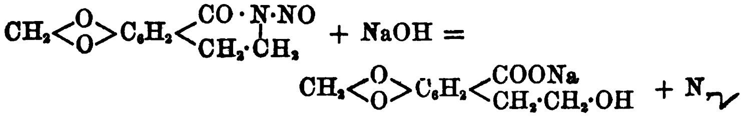
After standing for some time, the precipitate is collected, washed several times with water, dried on a porous plate, and recrystallised once or twice from alcohol. The pure substance is thus obtained in long, deep-yellow needles, which on analysis gave the following numbers:—

0·1575 gram substance gave 0·0580 gram H_2O and 0·3150 gram CO_2.

0·1003 gram substance gave 10·7 c.c. N; $t = 17°$; bar. = 760 mm.

	Theory. $C_{10}H_8N(NO)O_3$.	Found.
C	54·54 per cent.	54·55 per cent.
H	3·63 „	4·04 „
N	12·73 „	12·70 „

This interesting substance crystallises from alcohol in beautiful, long, glistening, yellow needles or four-sided prisms which melt at 194—195° with decomposition. It is readily soluble in boiling alcohol, chloroform, and benzene, almost insoluble in water or light petroleum, and very sparingly soluble in bisulphide of carbon. The solubility of this compound in solvents is very much influenced by its condition, the amorphous substance being far more readily dissolved than the crystalline variety. It is insoluble in acids and alkalis in the cold, but it dissolves readily in warm dilute sodium hydrate solution with evolution of nitrogen and formation of a salt of ω-hydroxyethylpiperonylcarboxylic acid, thus:—



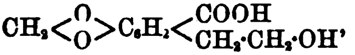
$$CH_2{<}{\substack{O\\O}}{>}C_6H_2{<}{\substack{CO\cdot N\cdot NO\\CH_2\cdot CH_2}} + NaOH = CH_2{<}{\substack{O\\O}}{>}C_6H_2{<}{\substack{COONa\\CH_2\cdot CH_2\cdot OH}} + N$$

a decomposition which is described in detail on p. 1020.

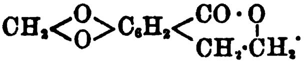
The least trace of the nitroso-derivative, when treated with phenol and two drops of sulphuric acid, gives a red solution, which, on the addition of excess of dilute alkali, changes to a beautiful blue (Liebermann's nitroso-reaction).

The nitroso-compound seems to be readily reduced in alcoholic solution by tin and hydrochloric acid, the original yellow solution becoming almost colourless. No attempts were made to isolate the reduction product.

ω-Hydroxyethylpiperonylcarboxylic Acid, $C_{10}H_{10}O_5$ =

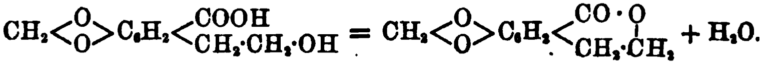


$CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{COOH}{CH_2\cdot CH_2\cdot OH}$, *and its Anhydride*, $C_{10}H_8O_4$ =



$CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{CO\cdot O}{CH_2\cdot CH_2}$.

As mentioned in the last paragraph, the nitroso-derivative, $C_{10}H_5N(NO)O_3$, is readily decomposed by boiling with alkalis with evolution of nitrogen, and formation of a salt of a new acid, $C_{10}H_{10}O_5$. The latter, on the addition of an acid, is precipitated in the form of slender, white needles, which are somewhat difficult to purify on account of the ease with which they are converted into the inner anhydride $C_{10}H_8O_4$, thus:—



$$CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{COOH}{CH_2\cdot CH_2\cdot OH} = CH_2<\genfrac{}{}{0pt}{}{O}{O}>C_6H_2<\genfrac{}{}{0pt}{}{CO\cdot O}{CH_2\cdot CH_2} + H_2O.$$

The best results were obtained by employing the crude amorphous nitroso-compound, as obtained directly by the action of sodium nitrite on the hydrochloric acid solution of the substance $C_{10}H_9NO_3$ (see p. 1019), as this is much more readily acted on by alkalis than is the crystalline product.

The yellow precipitate is well washed, mixed with a considerable quantity of water (3 grams of nitroso-compound to 100 c.c. of water), transferred to a porcelain basin, sufficient sodium hydrate added to make the liquid very distinctly alkaline, and the whole gently heated on a water bath. In a short time decomposition sets in, and the nitroso-compound rapidly disappears, considerable quantities of nitrogen being evolved. The product, if not quite clear, is filtered, well cooled, acidified with hydrochloric acid, and allowed to stand for about half an hour. The white, crystalline precipitate, which consists of the nearly pure acid $C_{10}H_{10}O_5$, is collected and well washed with small quantities of water, care being taken to preserve all the aqueous solutions, as these, when extracted with ether, yield further quantities of the acid. The purification of the acid $C_{10}H_{10}O_5$ is best accomplished by first converting it into its anhydride, $C_{10}H_8O_4$, recrystallising this several times, and then reconverting the pure anhydride into the acid by dissolving it in alkali, and reprecipitating with hydrochloric acid.

For this purpose, the crude acid is dissolved in the least possible quantity of boiling water, the solution gently boiled for about five minutes, and rapidly filtered through a jacketed funnel. The hot liquid, on cooling, deposits beautiful, glistening, colourless crystals of the anhydride $C_{10}H_8O_4$, which by recrystallisation from water are readily obtained pure. For analysis, the substance was dried at 105°.

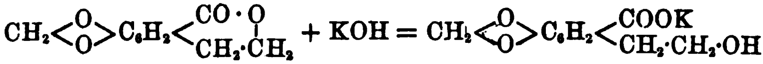
I. 0·1582 gram substance gave 0·0614 gram H_2O and 0·3620 gram CO_2.

II. 0·1418 gram substance gave 0·0540 gram H_2O and 0·3252 gram CO_2.

	Theory. $C_{10}H_8O_4$.		Found. I.	Found. II.	
C	62·50	per cent.	62·40	62·54	per cent.
H	4·17	,,	4·31	4·23	,,
O	33·33	,,	33·29	33·23	,,

This anhydride, $C_{10}H_8O_4$, melts at 126—127°, and distils without decomposition when heated in small quantities. It is readily soluble in boiling water, and the hot solution on cooling deposits the substance in the form of beautiful, glistening crystals, which, however, as a rule, are ill-defined. It is sparingly soluble in cold water, and is readily extracted from its solution by ether. It is, further, readily soluble in alcohol, ether, and acetic acid, excessively soluble in chloroform. It dissolves sparingly in cold benzene and light petroleum.

The anhydride $C_{10}H_8O_4$ is insoluble in alkaline carbonates in the cold, and is only very slowly dissolved on boiling, but it dissolves in ammonia, and much more readily in potassium hydrate solution with formation of the potassium salt of the acid $C_{10}H_{10}O_5$,



$$CH_2<\substack{O\\O}>C_6H_2<\substack{CO\cdot O\\CH_2\cdot CH_2} + KOH = CH_2<\substack{O\\O}>C_6H_2<\substack{COOK\\CH_2\cdot CH_2\cdot OH}$$

In studying this reaction, the pure anhydride $C_{10}H_8O_4$ was ground up with a little water into a thin paste, a few drops of a clear solution of potassium hydrate added, and the whole gently warmed until complete solution had taken place. The solution was nearly neutralised with dilute hydrochloric acid, well cooled, an excess of acid added, the white, crystalline substance which separated collected, well washed with water, and dried on a porous plate, first at the ordinary temperature and then for a few minutes at 80°.

Analysis:—

0·1199 gram substance gave 0·0528 gram H_2O and 0·2510 gram CO_2.

	Theory. $C_{10}H_{10}O_5$.	Found.
C	57·14 per cent.	57·09 per cent.
H	4·77 ,,	4·87 ,,
O	38·09 ,,	38·04 ,,

ω-Hydroxyethylpiperonylcarboxylic acid melts at 146°, and is at the same time decomposed into its anhydride, $C_{10}H_8O_4$, and water. It is readily soluble in hot water, but sparingly so in cold. It may be recrystallised from warm water if the operation be quickly carried out, but boiling with water completely decomposes it, and the solution on cooling deposits the pure anhydride $C_{10}H_8O_4$. The acid is readily soluble in hot and cold alcohol, ether, and chloroform, but only sparingly in cold benzene and light petroleum. The dry substance may be heated at 100° for some time without undergoing much decomposition, but at a temperature of 120—130° it rapidly liquefies, and is soon completely converted into its anhydride. The acid dissolves very readily in concentrated solutions of hydrogen iodide or bromide, and on gently warming it is very rapidly converted into the anhydride, which, on the addition of water, separates in plates. The acid does not combine with hydroxylamine.

The dissociation constant for the electric conductivity of the acid $C_{10}H_{10}O_5$ at different concentrations was kindly determined by Dr. Walker and found to be $K = 0·0081$. The acid is therefore stronger than benzoic acid, and about as strong as metahydroxybenzoic acid or orthomethoxybenzoic acid.

The solution of the pure substance in dilute sodium carbonate does not decolorise potassium permanganate except after long standing, a proof that the acid is not unsaturated (compare Baeyer, *Annalen*, **245**, 146). An aqueous solution of the acid is not precipitated by lead acetate, neither does it reduce ammoniacal nitrate of silver or Fehling's solution.

Fusion of the Acid $C_{10}H_{10}O_5$ *with Potash.*—1 gram of the pure substance was dissolved in concentrated aqueous potassium hydrate, the solution evaporated in a silver basin, and heated at 180° for about 10 minutes. Water was added, the clear solution acidified, and extracted four times with ether. The ethereal solution, on evaporation, deposited a small quantity of a light brown oil, which was very soluble in water; the solution gave with ferric chloride a deep green coloration and other reactions characteristic of a catechol derivative.

Oxidation of the Acid $C_{10}H_{10}O_5$.—A large number of experiments were made on the action of oxidising agents on this acid, as it appeared probable that in this way some clue to its constitution might be obtained. 2 grams of the pure substance was dissolved in dilute sodium hydrate, and a very dilute solution of potassium permanganate (5 grams) run in in the cold. Oxidation took place at once with formation of a brown solution, but no hydrated oxide of manganese was precipitated until the liquid was boiled. The product was filtered, the clear solution evaporated to a small bulk, and acidified with dilute hydrochloric acid. A white, crystalline precipitate separated at once, which weighed 1·2 grams, and consisted of the pure acid $C_{10}H_{10}O_5$.

Analysis:—

0·1678 gram substance gave 0·0740 gram H_2O and 0·3514 gram CO_2.

	Theory. $C_{10}H_{10}O_5$.	Found.
C	57·14 per cent.	57·11 per cent.
H	4·77 „	4·89 „

The filtrate from these crystals was repeatedly extracted with ether, and on evaporating the ethereal solution a colourless oil remained which solidified on standing; on recrystallisation from water, it melted at 126°, and consisted of the anhydride $C_{10}H_8O_4$. No other product could be isolated. It is probable, therefore, that the oxidation completely destroys part of the substance, leaving the remainder untouched. This experiment was repeated several times under the most varied conditions, but always with the same result.

Negative results were also obtained on using dilute nitric acid, iodine and sodium carbonate, and chromic acid as oxidisers.

Salts of Hydroxyethylpiperonylcarboxylic Acid.

In order, in the first place, to determine the basicity of this acid, the pure anhydride was dissolved in excess of standard potassium hydrate solution, a trace of phenolphthaleïn added, and the solution neutralised with standard sulphuric acid:—

0·63 gram of substance required for neutralisation 33·8 c.c. of standard potassium hydrate solution, containing in 1 c.c. 0·005461 gram KOH; the amount required for neutralisation was therefore 0·185 gram KOH. This proves that the acid is monobasic, as on this assumption 0·184 gram KOH would be required for neutralisation.

Silver Salt, $C_{10}H_9O_5Ag$.—The preparation of a sample of this salt pure enough for analysis was attended with considerable difficulty. The preparation which gave the best results was obtained by dissolving the acid in a slight excess of ammonia, removing the excess by allowing the solution to stand over sulphuric acid until nearly neutral, and then precipitating the slightly alkaline solution by nitrate of silver. The white, crystalline precipitate was well washed, and dried on a porous plate over sulphuric acid under reduced pressure.

Analysis:—

0·2651 gram substance gave 0·0720 gram H_2O, 0·3730 gram CO_2, and 0·0894 gram Ag.

	Theory. $C_{10}H_9O_5Ag$.	Found.
C	37·85 per cent.	38·34 per cent.
H	2·84 „	3·02 „
Ag	34·07 „	33·72 „

Other analyses gave similar results, the carbon and hydrogen determinations being always too high, the silver determination too low; in one or two cases, the silver was found as low as 30—31 per cent. The explanation of this is that the silver salt always contained small quantities of the anhydride $C_{10}H_8O_4$, and it is extremely probable that perfectly accurate numbers might be obtained by dissolving the acid in dilute potassium hydrate solution, neutralising with dilute nitric acid, and then precipitating with silver nitrate (compare Salts of Berberilic Acid, p. 1049). The silver salt is crystalline, and moderately soluble in hot water.

A moderately dilute solution of the ammonium salt showed the following behaviour with reagents:—

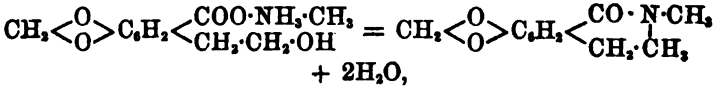
Copper Sulphate.—A dark green precipitate readily soluble in hot water.

Lead Acetate.—A white precipitate readily soluble in hot water.

Zinc Sulphate.— } No precipitate.
Cadmium Chloride.— }
Barium Chloride.— }

The *potassium salt* may be obtained in long needles by dissolving the anhydride $C_{10}H_8O_4$ in a warm and strong solution of pure potassium hydrate, and allowing the clear solution to cool slowly.

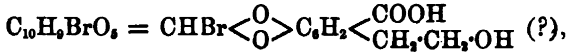
The *methylamine salt* was prepared by dissolving the pure acid in a slight excess of an aqueous solution of methylamine, and allowing the solution to evaporate over sulphuric acid under reduced pressure. A thick, oily residue was obtained which slowly crystallised. This salt was prepared, because it was thought very probable that on dry distillation it would yield oxyhydrastinine and water, thus:—



$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}COO\cdot NH_3\cdot CH_3\\CH_2\cdot CH_2\cdot OH\end{matrix} = CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}CO\cdot N\cdot CH_3\\CH_2\cdot CH_2\end{matrix} + 2H_2O,$$

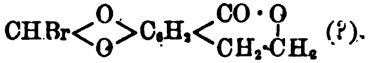
a decomposition which would be of considerable theoretical interest. The salt was rapidly distilled from a small retort, quantities of steam and methylamine were evolved, and an oily distillate was obtained, which, on cooling, solidified to a hard cake of crystals. These, after recrystallisation from water, melted at 126°, and showed all the properties of the anhydride $C_{10}H_8O_4$, and no trace of oxyhydrastinine could be isolated.

ω-Hydroxyethylbromopiperonylcarboxylic acid,



$$C_{10}H_9BrO_5 = CHBr{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{COOH}{CH_2\cdot CH_2\cdot OH}\ (?),$$

and its Anhydride, $C_{10}H_7BrO_4$ =



$$C_{10}H_7BrO_4 = CHBr{<}\genfrac{}{}{0pt}{}{O}{O}{>}C_6H_2{<}\genfrac{}{}{0pt}{}{CO\cdot O}{CH_2\cdot CH_2}\ (?).$$

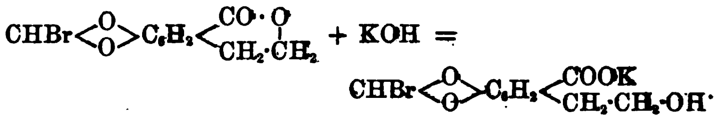
The bromination of the anhydride $C_{10}H_8O_4$ is readily accomplished by exposing the finely-divided substance to bromine vapour under a bell jar, in the presence of direct sunlight. After standing for three days, a dark-brown semi-solid mass is obtained, which is freed from excess of bromine by exposure to a current of air, and then ground up with a little alcohol in a mortar. This treatment removes a quantity of dark-coloured impurity, leaving behind an almost colourless powder, which, after repeated recrystallisation from alcohol, is readily obtained pure in the form of colourless needles. For analysis, the substance was dried at 110°:—

0·2015 gram substance gave 0·0480 gram H_2O and 0·3248 gram CO_2.

0·2340 gram substance, heated in a sealed tube with nitric acid and nitrate of silver at 120—130° for four hours, gave 0·1638 gram AgBr.

	Theory. $C_{10}H_7BrO_4$.	Found.
C	44·28 per cent.	43·96 per cent.
H	2·47 „	2·64 „
Br........	29·52 „	29·76 „

This new substance melts at 146—147°. It is readily soluble in hot benzene and hot alcohol, excessively soluble in chloroform, moderately so in carbon bisulphide, but only sparingly in light petroleum or water. It crystallises from alcohol in wooly needles, from carbon bisulphide in hard balls of needles. It is insoluble in alkalis and alkaline carbonates in the cold, and is only very slowly decomposed even on long boiling with sodium hydrate solution. Alcoholic potash, on the other hand, readily dissolves it with formation of the potassium salt of ω-hydroxyethylbromopiperonylcarboxylic acid, thus :—



$$CHBr\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}CO\cdot O\\CH_2\cdot CH_2\end{matrix}\right. + KOH = CHBr\left<\begin{matrix}O\\O\end{matrix}\right>C_6H_2\left<\begin{matrix}COOK\\CH_2\cdot CH_2\cdot OH\end{matrix}\right.$$

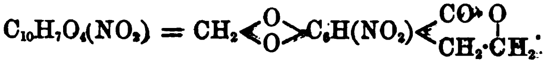
2 grams of the pure compound $C_{10}H_7BrO_4$ was mixed with a little methyl alcohol, a considerable excess of methyl alcoholic potash added, and the whole heated to boiling. In a short time the crystals had entirely dissolved, but almost immediately afterwards a quantity of a white, crystalline substance separated, which was the potassium salt of the new acid $C_{10}H_9BrO_5$. Sufficient hot water was added to bring this again into solution, the liquid boiled to expel the methyl alcohol, and the well-cooled solution acidified with dilute hydrochloric acid. The very voluminous amorphous precipitate thus produced was collected, washed with water, dried on a porous plate, and dissolved in a little boiling 80 per cent. methyl alcohol. This solution on cooling deposited the new compound in the form of beautiful, colourless needles, which, after washing with methyl alcohol and drying first on a porous plate and then for a short time at 80°, gave the following numbers on analysis :—

0·1654 gram substance gave 0·0480 gram H_2O and 0·2505 gram CO_2.

	Theory. $C_{10}H_9BrO_5$.	Found.
C	41·52 per cent.	41·31 per cent.
H	3·11 „	3·27 „

This acid melts at 146—147°, and is at the same time decomposed into water and the anhydride $C_{10}H_7BrO_4$. It is readily soluble in hot alcohol, but is almost completely deposited on cooling ; it is sparingly soluble in benzene, light petroleum, chloroform, and hot water, almost insoluble in cold water. It dissolves very readily in fuming hydriodic acid, but not in fuming hydrochloric acid. It dissolves with great ease in alkalis and alkaline carbonates, but no salts have been analysed. The potassium salt crystallises from water, in which it is not very soluble, in long, slender needles. The acid $C_{10}H_9BrO_5$ dissolves readily in warm concentrated nitric acid, forming a deep-red solution, which, on warming, gets darker and darker until ultimately oxidation sets in. Water precipitates from this solution a salmon-coloured mass, which crystallises from alcohol, in which it is sparingly soluble, in slender needles; these turn dark at 250° without melting. This substance contains both nitrogen and bromine ; it is insoluble in cold potassium hydrate, but on warming it dissolves forming an intense reddish-violet solution. This compound is most probably *ω-hydroxyethylbromonitropiperonylcarboxylic anhydride*, $C_{10}H_6Br(NO_2)O_4$.

ω-Hydroxyethylnitropiperonylcarboxylic Anhydride,



$$C_{10}H_7O_4(NO_2) = CH_2<\begin{matrix}O\\O\end{matrix}>C_6H(NO_2)<\begin{matrix}CO\cdot O\\ CH_2\cdot CH_2\end{matrix}.$$

The anhydride $C_{10}H_8O_4$ dissolves readily in concentrated nitric acid, forming a deep reddish-brown solution; on the addition of water, a yellow, crystalline precipitate is obtained, which consists of the almost pure nitro-compound. The precipitate was collected, washed with water, dissolved in boiling water, and filtered from a small quantity of insoluble matter. The clear solution, after a time, deposited long, thin, yellowish needles, which, after well washing and drying at 100°, gave the following numbers on analysis:—

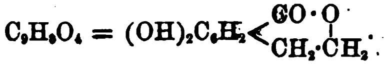
0·1524 gram substance gave 0·0430 gram H_2O and 0·2840 gram CO_2.

0·1830 gram substance gave 9·6 c.c. N; $t = 18°$; bar. = 759 mm.

	Theory. $C_{10}H_7O_4NO_2$.	Found.
C........	50·63 per cent.	50·82 per cent.
H........	2·95 „	3·13 „
N........	5·90 „	6·17 „

This nitro-derivative melts at 197°. It is readily soluble in hot water and alcohol, but only sparingly in these liquids in the cold. It is also sparingly soluble in benzene and light petroleum. It is insoluble in sodium hydrate solution in the cold, but on warming it dissolves, forming a deep yellow solution, which rapidly darkens, becoming dark brown and ultimately of a beautiful violet colour. Acids destroy this colour, but it reappears on the addition of an alkali.

ω-Hydroxyethylcatecholcarboxylic Anhydride,



$$C_9H_8O_4 = (OH)_2C_6H_2<\begin{matrix}CO\cdot O\\ CH_2\cdot CH_2\end{matrix}.$$

When heated in sealed tubes with dilute hydrochloric, hydrobromic, or hydriodic acid at 180°, or with distilled water at 210°, *ω*-hydroxyethylpiperonylcarboxylic anhydride, $C_{10}H_8O_4$, is decomposed, a deposit of carbon being formed on the sides of the tube. In all these cases ether extracts from the filtered solution a sticky substance; this dissolves readily in water and gives with ferric chloride an intense green coloration, which becomes violet and, finally, red on the addition of sodium hydrogen carbonate. This behaviour shows conclusively that the anhydride $C_{10}H_8O_4$ must be a derivative of catechol, in which the hydroxyl hydrogens are substituted, probably by two methyl groups or by the methylene group.

In order to determine whether methoxy-groups were present in the molecule, 0·2345 gram of the substance was introduced into a Zeisel's apparatus (*Monatsh.*, 6, 995) and heated with hydriodic acid, but, even after two hours, no trace of methyl iodide had been evolved, as shown by the fact that the alcoholic silver nitrate employed remained perfectly clear throughout. This proves that the substance $C_{10}H_8O_4$ contains no methoxy-group.

As all attempts to isolate the product of the reaction from the residual hydriodic acid solution gave unsatisfactory results, a large number of experiments on the action of hydrobromic and hydrochloric acids on the anhydride $C_{10}H_8O_4$ were made, the strength of the acids and the temperature of the decomposition being varied in each case. It was soon found that the product of the reaction could only be satisfactorily isolated when the strength of the acid (hydrochloric acid gave the best results) and the range of the temperature were kept within narrow limits. By carefully observing the following conditions excellent results were obtained:—

1 gram of the anhydride $C_{10}H_8O_4$ was ground up, mixed with 40 c.c. of water, 10 c.c. of ordinary concentrated hydrochloric acid (sp. gr. 1·168) added, and the mixture heated in a sealed tube for five hours at 170—175°.

The tube, which on cooling opened without pressure, was found to be filled with light flocks of charcoal, most of which adhered firmly to the under side of the tube. These were filtered off and the resulting almost colourless solution extracted six times with pure ether. The ethereal solution, after drying over calcium chloride and evaporating, deposited an almost colourless, crystalline residue. This was dissolved in a small quantity of hot water, the solution filtered into a glass dish, and allowed to evaporate to a small bulk over sulphuric acid under reduced pressure at the ordinary temperature. After standing for some time, the new substance separated in peculiar, hard, nodular masses, which were collected, washed with a little water, and dried at 100°.

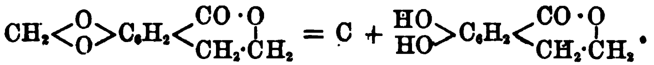
The analyses gave the following results:—

I. 0·1618 gram substance gave 0·0686 gram H_2O and 0·3542 gram CO_2.

II. 0·1316 gram substance gave 0·0554 gram H_2O and 0·2892 gram CO_2.

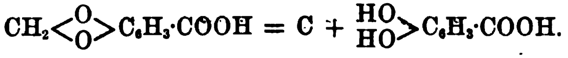
	Theory.	Found.	
	$C_9H_8O_4$.	I.	II.
C	60·00 per cent.	59·71	59·93 per cent.
H	4·44 ,,	4·71	4·67 ,,
O	35·55 ,,	35·58	35·40 ,,

This substance is formed from the anhydride $C_{10}H_8O_4$ by the simple separation of carbon, thus:—



$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\cdot O\\CH_2\cdot CH_2\end{matrix} = C + \begin{matrix}HO\\HO\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\cdot O\\CH_2\cdot CH_2\end{matrix}.$$

When heated in a capillary tube, it becomes soft at 210° and melts, not very sharply, at 220—225°. It is readily soluble in hot and cold water, and much more so than either of the substances $C_{10}H_8O_4$ or $C_{10}H_{10}O_6$; it is moderately soluble in methyl and ethyl alcohols, sparingly in benzene and chloroform. It dissolves readily in cold dilute caustic potash solution, forming a yellowish-coloured liquid. Its aqueous solution, with acetate of lead, gives a white, amorphous precipitate, soluble in much hot water; it also reduces ammoniacal nitrate of silver solution and Fehling's solution very rapidly in the cold. A drop of ferric chloride solution added to the aqueous solution produces at once an intense green coloration, which, on the careful addition of sodium hydrogen carbonate, gradually turns violet and finally deep red. The decomposition of the anhydride $C_{10}H_8O_4$, on heating with dilute hydrochloride acid, into $C_9H_8O_4$ and carbon is exactly similar to the change which piperonylic acid undergoes under like conditions. Fittig and Remsen (*Annalen*, **159**, 139) have shown that this acid, when heated at 170° with dilute hydrochloric acid, is converted into protocatechuic acid, with deposition of charcoal, thus:—



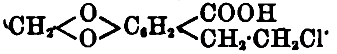
$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_3\cdot COOH = C + \begin{matrix}HO\\HO\end{matrix}{>}C_6H_3\cdot COOH.$$

Piperonylic acid. Protocatechuic acid.

The compound $C_{10}H_8O_4$ is, therefore, a piperonyl derivative, and the above experiment gave the first important clue as to the constitution of this substance and its derivatives.

Action of Phosphorus Pentachloride on the Anhydride $C_{10}H_8O_4$.

ω-Chlorethylpiperonylcarboxylic Acid, $C_{10}H_9ClO_4$ =

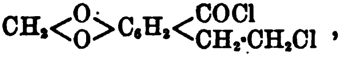


$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}COOH\\CH_2\cdot CH_2Cl\end{matrix}$$

In order to obtain some further clue to the constitution of the anhydride $C_{10}H_8O_4$, a very careful examination of the action of phosphorus pentachloride on this compound was undertaken.

2 grams of the pure dry substance was dissolved in 25 grams of chloroform, and then 3 grams of powdered pentachloride of phosphorus added. Scarcely any action took place in the cold, but on heating on a water-bath, considerable quantities of hydrogen chloride were evolved. The mixture, after gently boiling on a reflux apparatus

for about half an hour, was cooled, 2 grams of phosphorus pentachloride added, and the heating continued for another half hour. The product on cooling deposited a quantity of yellowish crystals, which readily dissolved again on warming. These crystals seemed to consist of the acid chloride,



$$\mathrm{CH_2}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{C_6H_2}<\substack{\mathrm{COCl}\\ \mathrm{CH_2\cdot CH_2Cl}},$$

mixed with small quantities of phosphorus pentachloride, but although several attempts were made to isolate the pure substance, no very satisfactory numbers could be obtained on analysis. That this acid chloride is contained in this product is proved by the decomposition which it undergoes on being mixed with methyl alcohol (see p. 1033).

In examining the product formed in the above reaction, the excess of chloroform was distilled off, the resulting brownish oil cautiously added to a quantity of powdered ice, and the whole allowed to stand until the phosphorus oxychloride and excess of pentachloride had been completely decomposed. The liquid was extracted three times with ether, the ethereal solution washed with water, dried over calcium chloride, and evaporated, when a thick, unpleasantly-smelling syrup was obtained which on standing solidified almost completely. The crystalline cake was well pressed to remove adhering oily matter, washed with a little 80 per cent. methyl alcohol, and dissolved in a small quantity of boiling chloroform. From this solution, the substance separated on cooling in long, thin, colourless needles, which after recrystallisation were readily obtained pure.

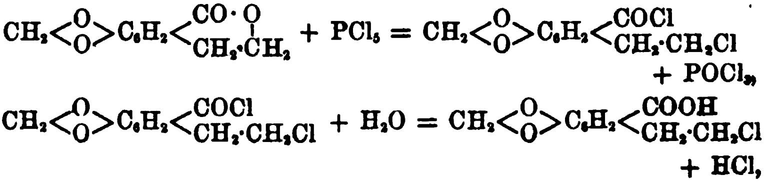
Analysis:—

0·1714 gram substance gave 0·0624 gram H_2O and 0·3310 gram CO_2.

0·2149 gram substance, heated in a sealed tube with nitric acid and nitrate of silver at 180° for four hours, gave 0·1315 gram AgCl.

	Theory. $C_{10}H_9O_4Cl$.	Found.
C	52·54 per cent.	52·66 per cent.
H	3·94 ,,	4·04 ,,
Cl	15·49 ,,	15·10 ,,

This substance $C_{10}H_9ClO_4$ is evidently formed from the anhydride $C_{10}H_8O_4$, as shown in the following equations:—

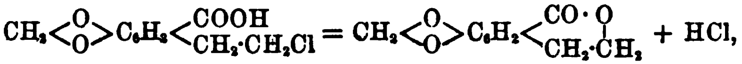


$$\mathrm{CH_2}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{C_6H_2}<\substack{\mathrm{CO\cdot O}\\ \mathrm{CH_2\cdot CH_2}} + \mathrm{PCl_5} = \mathrm{CH_2}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{C_6H_2}<\substack{\mathrm{COCl}\\ \mathrm{CH_2\cdot CH_2Cl}} + \mathrm{POCl_3},$$

$$\mathrm{CH_2}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{C_6H_2}<\substack{\mathrm{COCl}\\ \mathrm{CH_2\cdot CH_2Cl}} + \mathrm{H_2O} = \mathrm{CH_2}<\substack{\mathrm{O}\\ \mathrm{O}}>\mathrm{C_6H_2}<\substack{\mathrm{COOH}\\ \mathrm{CH_2\cdot CH_2Cl}} + \mathrm{HCl},$$

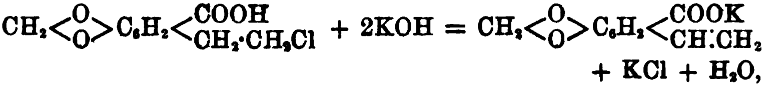
the acid chloride first formed being further decomposed on pouring the product into water. The substance $C_{10}H_9ClO_4$ crystallises from chloroform in long, thin, prismatic needles, which grow to a considerable length if the solution is allowed to cool slowly. It melts at 158—159° with decomposition, is readily soluble in ether, methyl and ethyl alcohols, and acetic acid, sparingly in water and cold chloroform. This latter property renders the separation of the chloride from any unchanged or regenerated anhydride $C_{10}H_8O_4$, with which the crude product is nearly always contaminated, a matter of no difficulty, as the latter is excessively soluble in chloroform.

The substance $C_{10}H_9ClO_4$ dissolves readily in alkalis and alkaline carbonates. When heated in the dry state, it decomposes at about 160°, with evolution of hydrogen chloride and formation of the anhydride $C_{10}H_8O_4$, thus:—



$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}COOH\\CH_2\cdot CH_2Cl\end{matrix} = CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\cdot O\\ \ \ |\\CH_2\cdot CH_2\end{matrix} + HCl,$$

a reaction very similar to that occurring in the formation of lactones from γ-halogen derivatives, *e.g.*, by the action of heat on γ-chlorobutyric acid (L. Henry, *Compt. rend.*, **101**, 1158—1161). When digested with alcoholic potash, the substance $C_{10}H_9ClO_4$ is readily decomposed with separation of potassium chloride. This reaction was studied in detail, because it was thought possible that an unsaturated derivative might result containing the side group $CH{:}CH_2$, thus:—



$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}COOH\\CH_2\cdot CH_2Cl\end{matrix} + 2KOH = CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}COOK\\CH{:}CH_2\end{matrix} + KCl + H_2O,$$

a decomposition which would be of considerable interest as determining the exact nature of the side chains in the compound $C_{10}H_8O_4$.

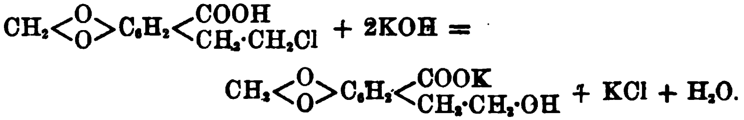
1 gram of the pure chloride was added to an excess of very strong alcoholic potash, and the whole boiled until the deposition of potassium chloride had ceased. The product was mixed with water, heated on a water-bath until free from alcohol, well cooled, and acidified with hydrochloric acid. The crystalline precipitate was collected, washed with water, and recrystallised from this solvent; when colourless needles were obtained which melted at 126° and showed all the properties of the anhydride $C_{10}H_8O_4$.

Analysis:—

0·1759 gram of substance gave 0·0663 gram H_2O and 0·4020 gram CO_2.

	Theory. $C_{10}H_8O_4$.	Found.
C........	62·50 per cent.	62·39 per cent.
H........	4·17 ,,	4·19 ,,

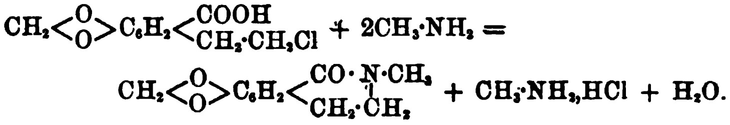
The regeneration of the anhydride $C_{10}H_8O_4$ in this reaction is easily accounted for by the following equation:—



$$CH_2<\substack{O\\O}>C_6H_2<\substack{COOH\\CH_2\cdot CH_2Cl} + 2KOH = CH_2<\substack{O\\O}>C_6H_2<\substack{COOK\\CH_2\cdot CH_2\cdot OH} + KCl + H_2O.$$

On acidifying with hydrochloric acid, the acid $C_{10}H_{10}O_5$ is precipitated, and this, on recrystallisation from water, is readily converted into its anhydride, $C_{10}H_8O_4$ (p. 1021).

As the experiments did not afford any clue to the nature of the side chains in the anhydride $C_{10}H_8O_4$, the action of methylamine on the compound $C_{10}H_9ClO_4$ was carefully studied. It seemed extremely probable that this reaction should lead to a synthesis of oxhydrastinine, thus:—



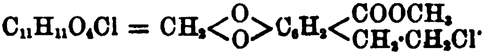
$$CH_2<\substack{O\\O}>C_6H_2<\substack{COOH\\CH_2\cdot CH_2Cl} + 2CH_3\cdot NH_2 = CH_2<\substack{O\\O}>C_6H_2<\substack{CO\cdot N\cdot CH_3\\CH_2\cdot CH_2} + CH_3\cdot NH_2,HCl + H_2O.$$

Oxyhydrastinine.

a synthesis which would at once prove the constitution of the anhydride $C_{10}H_8O_4$. This experiment was repeated several times under the most varied conditions, and great care was taken to exclude every trace of water, but in all cases an almost quantitative yield of the anhydride $C_{10}H_8O_4$ was obtained, the methylamine acting obviously much in the same way as alcoholic potash.

Similar results were obtained in experiments on the reduction of the chloride $C_{10}H_9ClO_4$ with zinc and acetic acid, and other reducing agents; the anhydride $C_{10}H_6O_4$ being the only product which could be isolated.

Methylic ω-Chlorethylpiperonylcarboxylate,



$$C_{11}H_{11}O_4Cl = CH_2<\substack{O\\O}>C_6H_2<\substack{COOCH_3\\CH_2\cdot CH_2Cl}.$$

This important substance has been prepared in considerable quantities for use in a number of synthetical experiments. It can be obtained in almost quantitative yield in the following way:—5 grams of the anhydride $C_{10}H_8O_4$ are dissolved in 30 grams of chloroform, 10 grams of powdered pentachloride of phosphorus added, and the mixture heated to boiling for half an hour in a reflux apparatus. The condenser is then removed, the chloroform boiled away, and the residual thick, oily mass, while still warm, poured in a thin stream into a considerable quantity of pure absolute methyl alcohol, the whole being well cooled during the operation. As soon as the very energetic reaction, which at once sets in, has subsided, the bulk of the methyl alcohol is distilled off, and the residue poured into cold water. The white, flocculent precipitate which separates is collected, well washed with water, dried on a porous plate, extracted with small quantities of boiling methyl alcohol, and the solution filtered from a small quantity of a white, insoluble substance. After distilling off the excess of methyl alcohol, the hot solution deposits, on cooling, long, beautiful, colourless needles of the nearly pure methyl salt. These were collected, recrystallised from methyl alcohol, and analysed with the following results:—

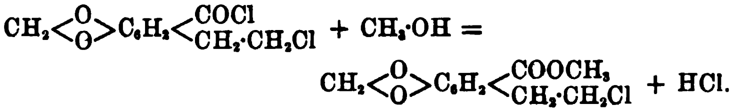
I. 0·1580 gram substance gave 0·0687 gram H_2O and 0·3144 gram CO_2.

0·1530 gram substance gave 0·2570 gram AgCl.

II. 0·1517 gram substance gave 0·0662 gram H_2O and 0·3030 gram CO_2.

	Theory.	Found.	
	$C_{11}H_{11}O_4Cl$.	I.	II.
C........	54·45 per cent.	54·27	54·47 per cent.
H........	4·54 „	4·82	4·84 „
Cl........	14·61 „	14·79	— „

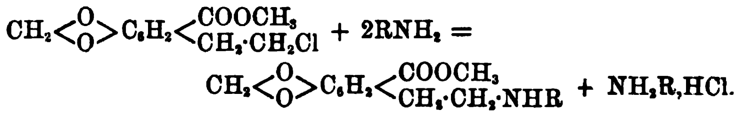
This methyl salt is obviously produced by the action of methyl alcohol on the acid chloride produced by the interaction of the phosphorus pentachloride and the anhydride $C_{10}H_8O_4$, thus:—



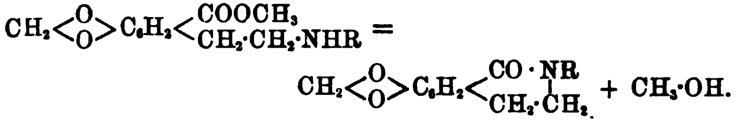
$$\mathrm{CH_2}\Big<\substack{\mathrm{O}\\ \mathrm{O}}\Big>\mathrm{C_6H_2}\Big<\substack{\mathrm{COCl}\\ \mathrm{CH_2\cdot CH_2Cl}} + \mathrm{CH_3\cdot OH} = \mathrm{CH_2}\Big<\substack{\mathrm{O}\\ \mathrm{O}}\Big>\mathrm{C_6H_2}\Big<\substack{\mathrm{COOCH_3}\\ \mathrm{CH_2\cdot CH_2Cl}} + \mathrm{HCl}.$$

The pure substance melts at 82—83°. It is readily soluble in benzene, light petroleum, methyl alcohol, and chloroform, sparingly in water, but excessively soluble in ether. It crystallises best from 80 per cent. methyl alcohol. It is readily hydrolysed by boiling with alcoholic potash, with regeneration of the acid $C_{10}H_{10}O_5$.

This methyl salt is of considerable value from a theoretical point of view, as when heated with primary amines it yields amido-derivatives, which, on hydrolysis with alcoholic potash, are converted into derivatives of isoquinoline, thus:—



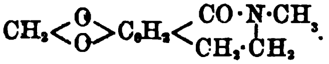
$$\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{COOCH_3}\\ \mathrm{CH_2\cdot CH_2Cl}\end{smallmatrix} + 2\mathrm{RNH_2} = \mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{COOCH_3}\\ \mathrm{CH_2\cdot CH_2\cdot NHR}\end{smallmatrix} + \mathrm{NH_2R,HCl}.$$



$$\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{COOCH_3}\\ \mathrm{CH_2\cdot CH_2\cdot NHR}\end{smallmatrix} = \mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{CO\cdot NR}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix} + \mathrm{CH_3\cdot OH}.$$

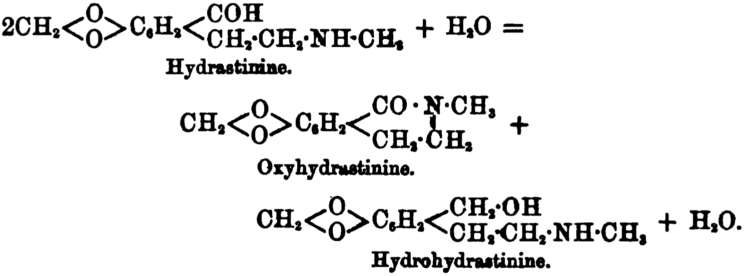
Thus, when heated with methylamine, oxyhydrastine is formed; a synthesis which at once proves the constitution of the anhydride $C_{10}H_8O_4$, and indirectly that of the substance $C_{10}H_9NO_3$ (see Introduction, p. 998). Similarly constituted isoquinoline derivatives have also been obtained by heating the methyl salt with aniline and with ethylamine, as will be described in the subsequent chapters.

Oxyhydrastinine, $C_{11}H_{11}NO_3$ =



$$\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{CO\cdot N\cdot CH_3}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix}.$$

This substance, which has been proved to have the constitution assigned to it above, was first obtained by Freund and Will (*Ber.*, **20**, 2401; compare Freund and Lachmann, *Ber.*, **22**, 2323) by the action of potassium hydrate on hydrastinine, thus:—



$$2\mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{COH}\\ \mathrm{CH_2\cdot CH_2\cdot NH\cdot CH_3}\end{smallmatrix} + \mathrm{H_2O} = \mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{CO\cdot N\cdot CH_3}\\ \mathrm{CH_2\cdot CH_2}\end{smallmatrix} + \mathrm{CH_2}{<}\begin{smallmatrix}\mathrm{O}\\ \mathrm{O}\end{smallmatrix}{>}\mathrm{C_6H_2}{<}\begin{smallmatrix}\mathrm{CH_2\cdot OH}\\ \mathrm{CH_2\cdot CH_2\cdot NH\cdot CH_3}\end{smallmatrix} + \mathrm{H_2O}.$$

Hydrastinine. Oxyhydrastinine. Hydrohydrastinine.

It may be obtained synthetically from methylic ω-chlorethylpiperonylcarboxylate by the action of methylamine in the following way:—

2 grams of the methylic salt were heated in a sealed tube with a strong alcoholic solution of methylamine (prepared by passing *dry* methylamine into absolute alcohol) for three hours at 100—120°, and then for three hours at 120—130°. The clear, almost colourless product was freed from excess of methylamine and from alcohol by evaporation, and the residue boiled for one hour with a strong alcoholic solution of potassium hydrate. Water was added, the alcohol driven off on a water-bath, and the product, which contained

oily drops, allowed to stand for 48 hours in a cool place; at the end of this time it was found that the oily drops had completely solidified. The hard, crystalline masses were collected, washed with water, freed from a trace of oily impurity by spreading on a porous plate, and purified by recrystallisation from dilute alcohol. In this way beautiful, colourless, glistening plates were obtained which, after drying first over sulphuric acid under reduced pressure and then at 80°, gave the following numbers on analysis:—

0·1562 gram substance gave 0·0798 gram H_2O and 0·3690 gram CO_2.

0·1366 gram substance gave 8·3 c.c. N; $t = 20°$; bar. = 740 mm.

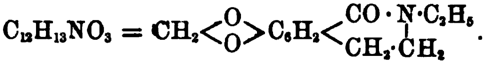
	Theory. $C_{11}H_{11}NO_3$.	Found.
C........	64·39 per cent.	64·43 per cent.
H........	5·36 „	5·67 „
N........	6·83 „	6·80 „

It melts at 97—98°, and is identical in all its properties with oxyhydrastinine.

The yield of this substance, obtained in the above reaction, is almost theoretical; but a very small quantity of an acid is also produced at the same time, which remains dissolved in the strong alkali, and may be extracted by ether after acidifying with hydrochloric acid. It was not further examined.

The synthesis of oxyhydrastinine from methylic ω-chlorethylpiperonylcarboxylate is readily understood by substituting CH_3 for R in the general equation, p. 1034.

Ethylamidoethylpiperonylcarboxylic Anhydride,



$$C_{12}H_{13}NO_3 = CH_2{<}\substack{O\\O}{>}C_6H_2{<}\substack{CO\cdot N\cdot C_2H_5\\ |\\ CH_2\cdot CH_2}.$$

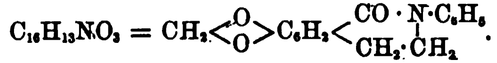
This may be prepared by the action of an alcoholic solution of ethylamine on methylic ω-chlorethylpiperonylcarboxylate, the method being similar to that employed in the synthesis of oxyhydrastinine. The product of the reaction, after boiling with alcoholic potash as described above, was a thick oil which, even on long standing, did not solidify. It was extracted from the alkaline liquors with pure ether, the ethereal solution washed, dried over calcium chloride, carefully filtered, and the ether evaporated. The residual, almost colourless oil was completely freed from moisture and ether by standing over sulphuric acid under reduced pressure, and then analysed with the following result:—

0·2264 gram substance gave 13·7 c.c. N; $t = 18°$; bar. = 746 mm.

	Theory. $C_{12}H_{13}NO_3$.	Found.
N	6·39 per cent.	6·80 per cent.

Ethylamidopiperonylcarboxylic anhydride is a colourless oil which, when heated in small quantities, distils almost undecomposed. The yield obtained in the above synthesis is almost quantitative, and the crude product evidently nearly pure.

Phenylamidoethylpiperonylcarboxylic Anhydride,



$$C_{16}H_{13}NO_3 = CH_2{<}^{O}_{O}{>}C_6H_3{<}\begin{matrix}CO\cdot N\cdot C_6H_5\\ CH_2\cdot CH_2\end{matrix}.$$

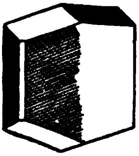
In preparing this substance, pure methylic ω-chlorethylpiperonylcarboxylate was dissolved in alcohol, excess of aniline added, and the mixture boiled in a reflux apparatus for half an hour. The alcohol was distilled off, the oily residue heated at 170—180° for half an hour, and the resulting dark-coloured mass hydrolysed by boiling with alcoholic potash. The product was mixed with water, the alcohol and excess of aniline driven off by distillation in a current of steam, and the residual liquid, which contained a dark-coloured, resinous substance, digested for five minutes with very dilute hydrochloric acid. The solid substance which separated was collected, washed with water, and ground up in a mortar with a little 80 per cent. alcohol. In this way a quantity of a dark, resinous substance was removed, leaving a brownish, crystalline mass; this, when dissolved in boiling alcohol, was deposited in beautiful glistening, colourless prisms as the solution cooled; the separation is very much hastened by the addition of a crystal of the crude substance.

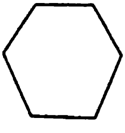
The analysis gave the following numbers:—

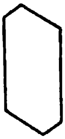
0·1927 gram substance gave 9·1 c.c. N; $t = 23°$; bar. = 746 mm.

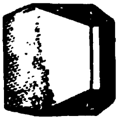
	Theory. $C_{16}H_{13}NO_3$.	Found.
N.... ...	5·24 per cent.	5·22 per cent.

This substance melts at 157°. It is very soluble in hot alcohol, benzene, and xylene, sparingly in water, cold alcohol, light petroleum, and carbon bisulphide, and exceedingly soluble in chloroform. Beautiful crystals are obtained by allowing the solution in benzene to evaporate spontaneously; these have the following forms:—

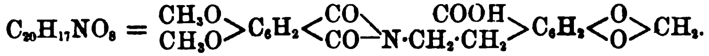








Anhydroberberilic Acid,



$$C_{20}H_{17}NO_8 = {CH_3O \atop CH_3O}>C_6H_2<{CO\diagdown \atop CO-}N\cdot{COOH \atop CH_2\cdot CH_2}>C_6H_2<{O \atop O}>CH_2.$$

This important compound is the principal constituent of the yellow precipitate obtained by the oxidation of berberine with potassium permanganate and subsequent treatment with sulphurous anhydride, as described on p. 1011. The methods employed in the isolation and purification of this substance are given in Part I of this research (*loc. cit.*, pp. 79 and 80).

Even after repeated recrystallisation from acetic acid, anhydroberberilic acid is almost always slightly discoloured by the presence of a very small quantity of a yellowish impurity which can only be completely removed with difficulty. On several occasions a beautifully pure product has been obtained by recrystallising the crude compound, first from large quantities of alcohol and then from glacial acetic acid.

An analysis confirmed the formula previously arrived at as representing the composition of this substance :—

0·1860 gram substance gave 0·0742 gram H_2O and 0·4095 gram CO_2.

0·2248 gram substance gave 7·1 c.c. N ; $t = 16°$; bar. = 740 mm.

	Theory. $C_{20}H_{17}NO_8$.	Found.	Mean of previous analyses.
C....	60·15 per cent.	60·04 per cent.	59·84 per cent.
H....	4·26 „	4·43 „	4·47 „
N....	3·51 „	3·53 „	3·54 „

Anhydroberberilic acid, when quite pure, is colourless, and has a most beautful, satiny lustre. It is very sparingly soluble in alkalis and alkaline carbonates in the cold, but when in a very finely-divided state (as obtained by grinding with water) it dissolves readily, even in alkaline carbonates at a temperature of 30—40°, and is reprecipitated unchanged on the addition of an acid. It therefore has acid properties, and is not a neutral substance, as was at first thought to be the case. In addition to the properties already given in Part I of this research, may be added that anhydroberberilic acid is not acted on by phenylhydrazine or by prolonged boiling with methyl iodide.

Salts of Anhydroberberilic Acid.

Very considerable difficulty was experienced in preparing salts directly derived from this acid, for the reason that when dissolved in ammonia or solutions of caustic alkalis, salts of berberilic acid (see p. 1048) are formed, thus :—

$$C_{20}H_{17}NO_8 + 2KOH = C_{20}H_{17}NO_9K_2 + H_2O.$$

It was, however, subsequently observed that the ammonium salt of berberilic acid, $C_{20}H_{17}NO_9(NH_4)_2$, on long standing over sulphuric acid in a vacuum, or much more rapidly on warming its aqueous solution, gradually gives off one-half of its ammonia, and yields the ammonium salt of anhydroberberilic acid, thus:—

$$C_{20}H_{17}NO_9(NH_4)_2 = C_{20}H_{16}NO_8(NH_4) + NH_3 + H_2O.$$

This salt, on the addition of an acid, now gives a precipitate of anhydroberberilic acid, instead of one of berberilic acid, as was the case at first.

This behaviour accounts for the fact that previously (Part I, p. 81) good numbers could not be obtained in the analysis of the silver salt prepared by precipitating a solution of the ammonium salt with silver nitrate. The analysis gave numbers lying between those required for the bibasic salt $C_{20}H_{17}NO_9Ag_2$ and those required for the monobasic salt $C_{20}H_{16}NO_8Ag$, showing that the bibasic ammonium salt used had already undergone some decomposition.

Silver Salt.—In re-examining the salts of anhydroberberilic acid, the pure substance was ground up with water to the consistency of a thin paste, rendered decidedly alkaline with ammonia, and gently warmed on a water-bath at 30—40° until the whole had dissolved. The solution was then placed in a dish over sulphuric acid in a vacuum, and allowed to evaporate almost to dryness. The gelatinous residue was dissolved in water with the aid of a drop of ammonia, heated at 60° on a water-bath for two or three hours, filtered, and the solution precipitated by silver nitrate in three fractions, at a temperature of about 40°, a preliminary precipitate of a small quantity being discarded. By this method the silver salt is obtained as a white, granular powder which is readily washed, whereas, if the precipitation takes place in the cold, the salt is gelatinous. The middle fraction was well washed with cold water, dried on a porous plate, first over sulphuric acid in a vacuum and then at 60°, and analysed with the following results:—

I. 0·1514 gram substance gave 0·0483 gram H_2O, 0·2620 gram CO_2, and 0·0328 gram Ag.

II. 0·2684 gram substance gave 0·0560 gram Ag.

	Theory. $C_{20}H_{16}NO_8Ag$.	Found. I.	 II.	
C........	47·43 per cent.	47·20	—	per cent.
H........	3·16 ,,	3·55	—	,,
Ag.......	21·34 ,,	21·66	20·86	,,

This silver salt is sparingly soluble in water, and very stable; even prolonged heating at 100° scarcely decomposes it; for ordinary purposes it may therefore be dried at 100°.

Copper Salt, $(C_{20}H_{16}NO_8)_2Cu + 2H_2O$.—This salt was obtained as a brilliant, light-blue precipitate by the addition of a solution of copper sulphate to the solution of the ammonium salt. It was well washed with water and dried over sulphuric acid in a vacuum.

Analysis:—

0·2632 gram substance, heated at 100° till the weight became constant, lost 0·0104 gram = 3·99 per cent.

$(C_{20}H_{16}NO_8)_2Cu + 2H_2O$ contains 4·02 per cent. Aq.

The dry substance (0·2528 gram), on ignition in a current of air, left 0·0247 gram CuO.

	Theory. $(C_{20}H_{16}NO_8)_2Cu$.	Found.
Cu.......	7·36 per cent.	7·79 per cent.

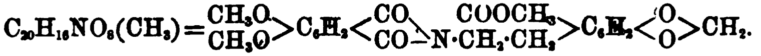
A dilute neutral solution of the ammonium salt shows the following behaviour with reagents:—

Cadmium Chloride.—A white, gelatinous precipitate.

Lead Acetate.—A white, gelatinous precipitate, somewhat soluble in hot water.

Barium and Calcium Chlorides.—No precipitates.

Methyl Salt of Anhydroberberilic Acid,



$$C_{20}H_{16}NO_8(CH_3) = \begin{matrix}CH_3O\\ CH_3O\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\diagdown\\ CO{-}\end{matrix}N\cdot\begin{matrix}COOCH_3\\ CH_2\cdot CH_2\end{matrix}{>}C_6H_2{<}\begin{matrix}O\\ O\end{matrix}{>}CH_2.$$

In order to be certain as to the basicity of anhydroberberilic acid, it was thought necessary to prepare some crystalline salt which could be readily purified, and from which trustworthy numbers could be obtained. As the metallic salts did not crystallise, and for this reason gave only imperfect numbers on analysis, attention was next directed to the preparation of a *methyl salt*. This salt is readily prepared by the action of methyl iodide on the silver salt, $C_{20}H_{16}NO_8Ag$. 2 grams of the pure dry silver salt was mixed with 20 c.c. of pure ether, a large excess of methyl iodide (5—10 grams) added, and the whole heated to boiling in a flask connected with a reflux apparatus. As soon as the decomposition was complete, the ether and excess of methyl iodide were distilled off, and the residue extracted three or four times with boiling absolute alcohol. The filtered extract, on evaporation, deposited an almost solid cake of the crude methyl salt; this was purified by spreading on a porous plate and subsequent recrystallisation, twice from alcohol and once from acetic acid. The beautifully white glistening crystalline powder thus obtained was dried at 100°, and analysed with the following results:—

I. 0·1352 gram substance gave 0·0601 gram H_2O and 0·3016 gram CO_2.
0·1783 gram substance gave 5·2 c.c. N; $t = 14°$; bar. = 740 mm.
II. 0·1670 gram substance gave 0·0710 gram H_2O and 0·3720 gram CO_2.
III. 0·1724 gram substance gave 0·0734 gram H_2O and 0·3844 gram CO_2.

	Theory.	Found.			
	$C_{20}H_{16}(CH_3)NO_8$.	I.	II.	III.	
C......	61·01 per cent.	60·84	60·75	60·81	per cent.
H......	4·60 „	4·93	4·72	4·73	„
N......	3·39 „	3·33	—	—	„

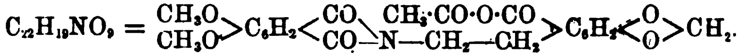
This methyl salt melts at 178—179°. In a finely-divided condition it is moderately soluble in carbon bisulphide, boiling benzene, and alcohol, but the crystals are only very sparingly soluble in these solvents. It crystallises best from acetic acid, being deposited as a fine, crystalline powder, which, when examined under the microscope, is seen to consist of four-sided plates with bevelled edges. This methyl salt is readily hydrolysed by boiling with hydrochloric acid or alcoholic potash. In order to make sure that it was in reality a methyl salt, and that the CH_3 group was not attached to the nitrogen atom in the molecule $C_{20}H_{17}NO_8$, the number of methoxy-groups which it contained was determined by Zeisel's method (*Monatsh.*, 6, 995).

0·3016 gram substance, when heated with fuming hydriodic acid (sp. gr. 1·96), and the resulting methyl iodide passed into an alcoholic solution of silver nitrate, gave 0·4982 gram AgI.

	Theory for 3(OCH_3) groups in $C_{20}H_{16}(CH_3)NO_8$.	Found.
(CH_3O)	22·52 per cent.	21·91 per cent.

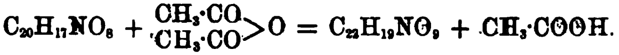
Three OCH_3 groups are therefore contained in this methyl salt, two from the original berberine molecule, and one in the form of $COOCH_3$; this substance is therefore the true methyl salt of anhydroberberilic acid.

Acetylanhydroberberilic Acid,



$$C_{22}H_{19}NO_9 = \begin{array}{l}CH_3O\\CH_3O\end{array}\!>C_6H_2<\begin{array}{l}CO\diagdown\ \ CH_3\cdot CO\cdot O\cdot CO\\CO\!-\!N\!-\!CH_2\!-\!CH_2\end{array}\!>C_6H_2<\begin{array}{l}O\\O\end{array}\!>CH_2.$$

Acetic anhydride reacts readily with anhydroberberilic acid with formation of an acetyl derivative, thus:—



$$C_{20}H_{17}NO_8 + \begin{array}{l}CH_3\cdot CO\\CH_3\cdot CO\end{array}\!>O = C_{22}H_{19}NO_9 + CH_3\cdot COOH.$$

In preparing this acetyl derivative, 2 grams of pure anhydroberberilic acid was mixed with 30 grams of acetic anhydride, and the mixture heated to boiling in a flask connected with a reflux apparatus for about three hours. The resulting brown solution, which was strongly fluorescent, was evaporated to a small bulk and allowed to stand for 12 hours. The crystals which separated were collected, washed with a little acetic anhydride, and recrystallised from this solvent. The acetyl derivative was thus obtained pure in hard, glistening, slightly yellowish prisms, which, after drying at 105° for two hours, gave the following results on analysis:—

0·1665 gram substance gave 0·0690 gram H_2O and 0·3644 gram CO_2.

0·3108 gram substance gave 9·4 c.c. N; $t = 8°$; bar. = 745 mm.

	Theory. $C_{22}H_{19}NO_9$.	Found.
C	59·82 per cent.	59·69 per cent.
H	4·28 „	4·60 „
N	3·17 „	3·51 „

Acetylanhydroberberilic acid melts at 139—140°, and at a higher temperature it decomposes with formation of an oil which smells strongly of acetic anhydride. It is very readily soluble in acetic acid, moderately in boiling alcohol, sparingly in boiling benzene and xylene, and almost insoluble in bisulphide of carbon and light petroleum. It crystallises from boiling xylene in peculiarly striated, needle-shaped crystals. The acid is very readily hydrolysed, boiling with water for a short time being sufficient to ensure complete decomposition into anhydroberberilic acid and acetic acid:—

$$C_{22}H_{19}NO_9 + H_2O = C_{20}H_{17}NO_8 + CH_3\cdot COOH.$$

The composition of the acetyl derivative may be accurately controlled by determining the amounts of these products produced on hydrolysis.

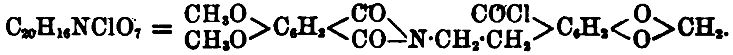
4·0610 grams of the pure substance was finely powdered and boiled in a flask connected with a reflux apparatus with 200 c.c. of 5 per cent. sulphuric acid. In a short time, complete hydrolysis had taken place with separation of colourless, flocculent masses of anhydroberberilic acid. These were collected on a filter, washed with water, and the yellow filtrate distilled in a current of steam until the distillate no longer showed any acid reaction. The acid liquid required for neutralisation 93 c.c. of standard solution of potassium hydrate (1 c.c. = 0·00598 gram of acetic acid).

This corresponds with 0·5561 gram of acetic acid = 13·7 per cent. According to the above equation, $C_{22}H_{19}NO_9$ gives 13·6 per cent.

The anhydroberberilic acid produced in this hydrolysis was very thoroughly washed with water until quite free from sulphuric acid, dried first on a plate and then at 100° until constant. It then weighed 3·688 grams = 90·8 per cent., whereas, according to the above equation, 90·5 per cent. should be produced.

These facts leave scarcely any doubt that the acetyl derivative is in reality a mixed anhydride of acetic and anhydroberberilic acids, and as such it has been represented at the head of this section. This accounts for the readiness with which it is decomposed into acetic and anhydroberberilic acids in contact with water.

Anhydroberberilic Chloride.



$$C_{20}H_{16}NClO_7 = {CH_3O \atop CH_3O}\!>\!C_6H_2\!<\!{CO \atop CO}\!\!>\!N{\cdot}CH_2{\cdot}CH_2\!<\!\!{COCl \atop }\!>\!C_6H_2\!<\!{O \atop O}\!>\!CH_2.$$

The action of phosphorus pentachloride on anhydroberberilic acid seems to be complicated, and the results obtained vary considerably with the quantity of the reagent employed and the subsequent treatment of the product.

Experiment I.—3 grams of pure anhydroberberilic acid was mixed with 50 grams of chloroform, and 6 grams of powdered phosphorus pentachloride added. As no action seemed to take place in the cold, the mixture was heated to boiling for half an hour; 2 grams more pentachloride added, and the heating continued for another half-hour. The residual light-brown liquid, which, on cooling, deposited a quantity of crystals, was, while still hot, transferred to a dish and freed from phosphorus oxychloride and excess of chloroform by heating on a water-bath. The yellow, crystalline residue was powdered, dissolved in boiling benzene, and the filtered solution allowed to stand 24 hours. In this way a considerable crop of garnet-coloured crystals was obtained, which, after repeated recrystallisation from benzene, gave the following numbers on analysis:—

0·1674 gram substance gave 0·0584 gram H_2O and 0·3540 gram CO_2.

0·3962 gram substance, heated with nitric acid and silver nitrate in a sealed tube at 180° for four hours, gave 0·1410 gram AgCl.

0·2984 gram substance gave 8·8 c.c. nitrogen; $t = 17°$; bar = 736 mm.

	Theory. $C_{20}H_{16}NClO_7$.	Found.
C	57·49 per cent.	57·70 per cent.
H	3·83 „	3·87 „
N	3·35 „	3·32 „
Cl........	8·50 „	8·74 „

This substance is the chloride of anhydroberberilic acid; its formation in the above reaction is represented by the equation

$$C_{20}H_{17}NO_8 + PCl_5 = C_{20}H_{16}NClO_7 + HCl + POCl_3.$$

This chloride melts at 167°, and is sparingly soluble in cold benzene, alcohol, and acetic acid. It crystallises from benzene in hard, thick, almost colourless prisms. It is practically insoluble in water, and for this reason is only very slowly acted on by this solvent. If, however, the powdered chloride is boiled with 80 per cent. acetic acid, it gradually dissolves, and, on cooling, anhydroberberilic acid crystallises out, thus:—

$$C_{20}H_{16}NClO_7 + H_2O = C_{20}H_{17}NO_8 + HCl.$$

The yield of crystalline chloride obtained in the above method of preparation is about 70 per cent. of the theoretical. A small quantity remains behind in the benzene mother liquors; by concentrating the solution, this may be recovered as a dark-coloured, crystalline mass, which is, however, difficult to purify.

Experiment II.—2 grams of anhydroberberilic acid, 12 grams of phosphorus oxychloride, and 6 grams of phosphorus pentachloride were mixed together and heated on a water-bath. In a short time the whole of the anhydro-acid dissolved, hydrogen chloride being liberated in abundance. After heating for an hour, 3 grams of phosphorus pentachloride was added, and the heating continued for another hour. The product, which, on cooling, solidified to a mass of crystals, was melted and poured, in a thin stream, into much water, the whole being kept as cool as possible during the operation. As soon as the energetic reaction, which at once sets in, had subsided, the brick-red precipitate which separated was collected, washed well, dried on a porous plate, and extracted with boiling alcohol. The greater part dissolved, leaving, however, a slight residue of regenerated anhydroberberilic acid. The alcoholic solution was evaporated to a small bulk and allowed to stand, when a brown, crystalline powder was obtained, which, after boiling in alcoholic solution with freshly ignited animal charcoal, and adding a little water, deposited an almost colourless, semi-crystalline precipitate. This was dissolved in alcohol, mixed with an equal bulk of water, and the solution allowed to stand exposed to the air. In a short time, crystalline crusts formed on the bottom of the dish, which, after well washing with dilute alcohol and drying over sulphuric acid in a vacuum, melted at 180—182°, and showed all the properties of berberilic acid (p. 1048).

The analysis gave confirmatory results:—

0·1439 gram substance gave 0·0619 gram H_2O and 0·3039 gram CO_2.

0·2059 gram substance gave 5·8 c.c. nitrogen; $t = 17°$; bar. = 745 mm.

	Theory. $C_{20}H_{19}NO_9$.	Found.
C	57·55 per cent.	57·59 per cent.
H	4·55 „	4·70 „
N	3·36 „	3·20 „

As anhydroberberilic acid is not attacked by dilute hydrochloric acid in the cold, it seems that under the above conditions phosphorus pentachloride converts anhydroberberilic acid into the chloride of berberilic acid, which, when mixed with water is decomposed with formation of berberilic acid, thus:—

$$C_{20}H_{17}NO_8 + PCl_5 = C_{20}H_{17}NO_7Cl_2 + POCl_3,$$
$$C_{20}H_{17}NO_7Cl_2 + 2H_2O = C_{20}H_{19}NO_9 + 2HCl.$$

Experiment III.—3 grams of anhydroberberilic acid were mixed with 40 grams of chloroform, 6 grams of phosphorus pentachloride added, and the mixture heated to boiling in a reflux apparatus for half an hour. The chloroform was then distilled off, and the residual hard cake of crystals broken up and shaken with a large quantity of water, the whole being well cooled during the operation. As soon as all action had subsided, the yellowish-brown precipitate was collected, dried on a porous plate, and dissolved in a large quantity of boiling ethyl alcohol.

The alcoholic solution was concentrated, allowed to stand for 24 hours, and the yellow crystals, which completely filled the liquid, collected, washed with a little alcohol, and dried on a porous plate. The fine, yellow, crystalline mass thus obtained contains two substances which are very readily separated by extraction with boiling benzene, in which the one present in the smallest quantity is very sparingly soluble. The insoluble substance was collected, dried at

100°, and recrystallised from acetic acid; the resulting crystalline mass melted at 236° and showed all the properties of anhydroberberilic acid. The filtrate from the crude anhydroberberilic acid was heated on a water-bath till free from benzene, and the residue recrystallised three times from alcohol.

The beautiful, pale yellow needles thus obtained were free from chlorine; they gave the following results on analysis:—

I. 0·1794 gram substance gave 0·0807 gram H_2O and 0·4064 gram CO_2

0·2813 gram substance gave 8·3 c.c. nitrogen; $t = 19°$; bar. = 740 mm.

II. 0·1696 gram substance gave 0·0775 gram H_2O and 0·3851 gram CO_2.

III. 0·1537 gram substance gave 0·0701 gram H_2O and 0·3483 gram CO_2.

IV. 0·1471 gram substance gave 0·0674 gram H_2O and 0·3335 gram CO_2.

	Theory.		Found.			
	$C_{20}H_{19}NO_7$.		I.	II.	III.	IV.
C......	62·33	per cent.	61·78	61·91	61·80	62·24 per cent.
H......	4·93	„	4·99	5·07	5·06	5·13 „
N......	3·63	„	3·35	—	—	— „

Each of these analyses was made with a different preparation.

This substance melts at 139—140°, it is readily soluble in hot alcohol, sparingly in the cold; the hot solution, on cooling, deposits the substance in beautiful, slender, pale-yellow needles. It is extremely soluble in benzene and chloroform, very sparingly in light petroleum, and the solutions show a beautiful fluorescence like that exhibited by solutions of quinine. It is insoluble in boiling dilute solutions of alkalis and alkaline carbonates and also in acids, but dissolves readily in warm alcoholic potash. As it seemed probable that this decomposition might throw some light on the constitution of this remarkable substance, about 1 gram was dissolved in dilute alcoholic potash, the solution heated to boiling for a few minutes, diluted with water, and the clear solution nearly neutralised and heated in an open basin on a water-bath until free from alcohol. The liquid was then well cooled, acidified with dilute hydrochloric acid, and the white, semi-solid precipitate which separated, collected, washed with water, and dried on a plate.

The hard mass thus obtained had all the properties of berberilic acid; it was identified by boiling with 50 per cent. sulphuric acid and collecting the crystalline precipitate of anhydroberberilic acid which formed. This, after recrystallisation from acetic acid, melted at 236°, and gave the following results on analysis:—

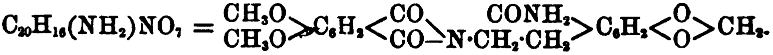
0·1510 gram substance gave 0·0630 gram H_2O and 0·3330 gram CO_2.

	Theory. $C_{20}H_{17}NO_8$.	Found.
C.........	60·15 per cent.	60·14 per cent.
H........	4·26 ,,	4·63 ,,

The formation of berberilic acid from a substance of the formula $C_{20}H_{19}NO_7$ by boiling with alcoholic potash is extremely difficult to understand, and although many experiments have been instituted, no clue to the constitution of this remarkable substance has, as yet, been found.

The amount of the substance $C_{20}H_{19}NO_7$ formed in the above decomposition varies very considerably; in some cases as much as 60 per cent. has been obtained, whereas in other experiments, conducted seemingly under exactly similar conditions, anhydroberberilic acid was the principal product.

Amide of Anhydroberberilic Acid,



$$C_{20}H_{16}(NH_2)NO_7 = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}CO\diagdown\\CO\!-\!\end{matrix}\!N\cdot\!\begin{matrix}CONH_2\\CH_2\cdot CH_2\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}O\\O\end{matrix}\!\!>CH_2.$$

The substance is readily prepared by the action of ammonia on the chloride of anhydroberberilic acid, thus:—

$$C_{20}H_{16}ClNO_7 + 2NH_3 = C_{20}H_{16}(NH_2)NO_7 + NH_4Cl.$$

The finely-divided chloride was mixed in a sealed tube with a large excess of a strong solution of ammonia in absolute alcohol. On standing in the cold, it was noticed that considerable decomposition took place, and after heating at 100° for five hours, the whole of the chloride had disappeared, and the tube was filled with feathery crystals of the amide. These were collected, washed with alcohol, and dissolved in a considerable quantity of 85 per cent. alcohol; this solution, on cooling, deposited beautiful, colourless, feathery crystals which, after drying at 100°, gave the following numbers on analysis:—

0·1446 gram substance gave 0·0638 gram H_2O and 0·3197 gram CO_2.
0·1888 gram substance gave 11·8 c.c. nitrogen; $t = 20°$; bar. = 746 mm.

	Theory. $C_{20}H_{16}(NH_2)NO_7$.	Found.
C........	60·30 per cent.	60·36 per cent.
H........	4·53 ,,	4·90 ,,
N........	7·03 ,,	7·01 ,,

This amide melts at 203°. It is readily soluble in boiling alcohol, but only sparingly in the cold; the hot solution, on cooling, deposits the substance as a very voluminous feathery mass, which, when dry, has a fine, satiny lustre.

The amide is insoluble in, and only very slowly hydrolysed by dilute acids; even boiling alcoholic hydrogen chloride seems to have little action on the substance. Alkalis on the other hand, act readily on the amide; on boiling with dilute alcoholic potash, the substance is readily dissolved with evolution of ammonia. The product was mixed with water, nearly neutralised with dilute hydrochloric acid, evaporated until free from alcohol, cooled, and acidified with dilute hydrochloric acid. The white, amorphous precipitate which separated, after being recrystallised from dilute alcohol, showed all the properties of berberilic acid:—

0·1820 gram substance gave 5·2 c.c. nitrogen; $t = 12°$; bar. = 740 mm.

	Theory. $C_{20}H_{19}NO_9$.	Found.
N	3·36 per cent.	3·38 per cent.

The decomposition of this amide into berberilic acid and ammonia by boiling with alcoholic potash takes place according to the equation

$$C_{20}H_{16}(NH_2)NO_7 + 2KOH = C_{20}H_{17}K_2NO_9 + NH_3.$$

Anilide of Anhydroberberilic Acid, $C_{20}H_{16}(NHC_6H_5)NO_7$.

The chloride of anhydroberilic acid reacts readily with aniline in the cold, with evolution of heat and formation of the corresponding anilide:—

$$C_{20}H_{16}ClNO_7 + 2NH_2C_6H_5 = C_{20}H_{16}(NH{\cdot}C_6H_5)NO_7 + C_6H_5NH_2HCl.$$

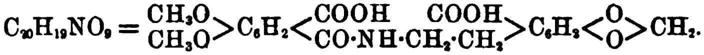
The finely-powdered chloride was mixed with an excess of pure aniline, allowed to stand for a few minutes, and then gradually heated to 180°. The resulting, almost colourless melt was poured in a thin stream into very dilute hydrochloric acid, the thick, oily precipitate well shaken and stirred until quite solid, collected, washed, and dissolved in boiling 90 per cent. alcohol. On cooling, this solution deposited the anilide in feathery tufts of fine needles. Analysis:—

0·2086 gram substance gave 11·3 c.c. nitrogen; $t = 22°$; bar. = 746 mm.

	Theory. $C_{20}H_{16}(NH{\cdot}C_6H_5)NO_7$.	Found.
N	5·91 per cent.	6·01 per cent.

The anilide melts at 199°. It is readily soluble in hot alcohol and benzene, sparingly in cold alcohol and carbon bisulphide, insoluble in water and light petroleum. It crystallises from alcohol in feathery tufts which, when dry, have a fine, satiny lustre and a distinct, blue fluorescence.

Berberilic Acid,



$$C_{20}H_{19}NO_9 = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COOH\quad\quad\quad\quad COOH\\CO\cdot NH\cdot CH_2\cdot CH_2\end{matrix}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2.$$

Although almost insoluble in alkalis in the cold, anhydroberberilic acid dissolves readily in dilute aqueous potassium hydrate at a temperature of 30—40° with formation of the potassium salt of berberilic acid :—

$$C_{20}H_{17}NO_8 + 2KOH = C_{20}H_{17}K_2NO_9 + H_2O.$$

In studying this decomposition, very carefully purified anhydroberberilic acid was ground up with water into a fine paste, warmed to about 35°, and potassium hydrate solution then run in, drop by drop, until the whole had dissolved. The clear solution was well cooled, nearly neutralised with hydrochloric acid, cooled again, filtered if necessary, and then an excess of dilute hydrochloric acid added, drop by drop, the liquid being well agitated after each addition. The white, semi-solid precipitate, thus thrown down, was collected, washed with water, and dried on a plate; this preparation consists of practically pure berberilic acid, and as such was employed in all future operations. Considerable difficulty was experienced in obtaining this acid in a crystalline condition; the best results were obtained by dissolving the acid in methyl alcohol, adding about an equal bulk of water, and allowing the solution to stand in an open dish exposed to the air. As the methyl alcohol evaporated, the acid was deposited in the form of a hard, crystalline cake on the bottom of the dish. This was washed with dilute methyl alcohol, dried on a porous plate, and analysed with the following result:—

I. 0·1649 gram substance gave 0·0752 gram H_2O and 0·3449 gram CO_2.

0·3090 gram substance gave 9·0 c.c. nitrogen; $t = 17°$; bar. = 740 mm.

II. 0·1320 gram substance gave 0·0590 gram H_2O and 0·2760 gram CO_2.

	Theory. $C_{20}H_{19}NO_9$.	Found. I.	Found. II.
C	57·55 per cent.	57·01	57·21 per cent.
H	4·55 ,,	5·06	4·96 ,,
N	3·36 ,,	3·30	— ,,

Berberilic acid melts at about 177—182°, being at the same time decomposed into water and anhydroberberilic acid :—

$$C_{20}H_{19}NO_9 = C_{20}H_{17}NO_8 + H_2O.$$

This melting point is only approximate, as the presence of even traces of impurity causes the substance to soften at a much lower temperature.

It is very readily soluble in methyl and ethyl alcohol. It dissolves appreciably in hot water, and if warm dilute solutions of the salts of the acid are precipitated and filtered, the clear filtrate gradually deposits colourless, granular masses of pure berberilic acid. When heated above its melting point, berberilic acid is completely converted into its anhydride, and the oily product on cooling solidifies to a transparent, fluorescent resin, which will remain in this condition for weeks; in contact with glacial acetic acid, however, this at once becomes crystalline, and after recrystallisation from this solvent, melts at 237°, and consists of pure anhydroberberilic acid.

Basicity of Berberilic Acid.—Two experiments were made with the object of determining the basicity of this acid.

Experiment I.—0·8629 gram of pure anhydroberberilic acid was ground up with water, mixed with 50 c.c. of standard potassium hydrate solution (1 c.c. = 0·005461 gram KOH), warmed to 35°, and kept at this temperature until complete solution had taken place. After the addition of a trace of phenolphthaleïn, 5 c.c. of standard sulphuric acid were required to completely neutralise the product. 0·8629 gram of substance required, therefore, for neutralisation 45 c.c. of potassium hydrate solution = 0·2457 gram KOH; whereas a bibasic acid, $C_{20}H_{19}NO_9$, requires for neutralisation 0·2422 gram KOH.

Experiment II.—0·5355 gram of berberilic acid required 26 c.c. of standard potassium hydrate solution for neutralisation = 0·1419 gram KOH. Theory for a bibasic acid, $C_{20}H_{19}NO_9$ = 0·1438 gram KOH.

Berberilic acid is therefore a *bibasic acid.*

Salts of Berberilic Acid.

Silver salt, $C_{20}H_{17}Ag_2NO_9$. This was prepared as follows:—Pure anhydroberberilic acid was dissolved in a dilute solution of pure potassium hydrate, titrated with dilute nitric acid until only very faintly alkaline, warmed to 30°, and a large excess of silver nitrate added, the whole being violently agitated during the addition. The resulting white precipitate was collected, well washed with water, and dried first on a porous plate over sulphuric acid in a vacuum, and then at 80°.

The analysis gave the following numbers:—

I. 0·2199 gram substance gave 0·0626 gram H_2O, 0·3108 gram CO_2, and 0·0761 gram Ag.

II. 0·2143 gram substance gave 0·0602 gram H_2O, 0·3036 gram CO_2, and 0·0726 gram Ag.

	Theory. $C_{20}H_{17}Ag_2NO_9$.	Found. I.	Found. II.
C........	38·08 per cent.	38·52	38·64 per cent.
H........	2·70 „	3·16	3·12 „
Ag.......	34·32 „	34·60	33·88 „

This silver salt is very sparingly soluble in water. It is very stable, and only very slowly acted on by light; it may be heated at 100° for a considerable time without undergoing decomposition.

The neutral solution of the potassium salt shows the following behaviour with reagents:—

Zinc Sulphate.—A white, gelatinous precipitate, moderately soluble in hot water, from which it separates on cooling as a white, amorphous mass.

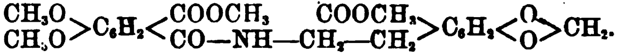
Copper Sulphate.—A light green precipitate, very sparingly soluble in water.

Cadmium Chloride.—A white, amorphous precipitate, soluble in hot water, separating out on cooling very much in the same way as the zinc salt.

Barium Chloride and *Calcium Chloride.*—No precipitate even on boiling.

The *ammonium salt* is mentioned on p. 1038, and its decomposition into ammonia and the ammonium salt of anhydroberberilic acid described.

Dimethyl Salt of Berberilic Acid, $C_{20}H_{17}(CH_3)_2NO_9$ =



$$\begin{array}{l}CH_3O\\CH_3O\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}COOCH_3\\CO-NH-CH_2-\end{array}\!\!\begin{array}{l}COOCH_3\\CH_2\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}O\\O\end{array}\!\!>CH_2.$$

This interesting salt is readily prepared by treating silver berberilate with excess of methyl iodide, thus:—

$$C_{20}H_{17}Ag_2NO_9 + 2CH_3I = C_{20}H_{17}(CH_3)_2NO_9 + 2AgI.$$

The pure dry silver salt was ground up, and heated with a large excess of methyl iodide and some pure ether for about two hours in a flask connected with a reflux apparatus. The ether and excess of methyl iodide were then distilled off, and the residue extracted three times with boiling absolute alcohol. The alcoholic solution was concentrated, and the crop of crystals which separated on standing, collected, washed with a little alcohol, and recrystallised from this solvent. The pure dimethyl salt was thus obtained in the form of long, thin, colourless needles, which, after drying at 100°, gave the following results on analysis :—

0·1590 gram substance gave 0·0756 gram H_2O and 0·3460 gram CO_2.

0·1966 gram substance gave 5·6 c.c. nitrogen ; $t = 24°$; bar. = 744 mm.

	Theory. $C_{20}H_{17}(CH_3)_2NO_9$.	Found.
C........	59·32 per cent.	59·24 per cent.
H........	5·17 „	5·28 „
N........	3·15 „	3·15 „

Dimethyl berberilate melts at 173—174°. It is readily soluble in hot methyl and ethyl alcohols, but only sparingly in the cold. The hot alcoholic solution, on cooling, deposits the substance in the form of a voluminous mass of snow-white needles, which when dry resemble cotton wool. The dimethyl salt is also readily soluble in hot benzene and xylene, very soluble even in cold chloroform, sparingly in light petroleum and carbon bisulphide. It is readily hydrolysed by boiling with alcoholic potash, with regeneration of berberilic acid.

Action of Heat on Berberilic Acid.

When heated to temperatures not greatly exceeding 180—190°, this acid is converted into anhydroberberilic acid, as already mentioned; but at higher temperatures a much more complicated decomposition sets in, which it is more difficult to follow.

In studying this change, 8 grams of the pure acid was melted in a flask heated in a paraffin-bath, and the temperature gradually raised to 250°, and kept at this for 10 minutes. Abundance of steam and some carbon dioxide were liberated, the substance became darker and darker, and on cooling solidified to a dark brown, almost black resin. This was dissolved in boiling glacial acetic acid, the solution separated from a small quantity of black, insoluble matter by filtration, and the acetic acid evaporated off on a water-bath. The residue was boiled with dilute potassium hydrate solution, which removes nearly all the black resin, leaving a light greenish powder. This was well washed, dried on a porous plate, and extracted with boiling light petroleum (b. p. 90—110°), filtered from insoluble matter, and allowed to stand for 24 hours. The almost colourless crystals which separated were recrystallised from water, dried at 100°, and analysed with the following result:—

I. 0·1612 gram substance gave 0·0740 gram H_2O and 0·3710 gram CO_2.

0·1715 gram substance gave 10·8 c.c. nitrogen; $t = 14°$; bar. = 746 mm.

II. 0·1495 gram substance gave 0·0679 gram H_2O and 0·3452 gram CO_2.

	Theory. $C_{10}H_9NO_3$.	Found.	
		I.	II.
C	62·82 per cent.	62·76	62·97 per cent.
H	4·71 „	5·10	5·04 „
N	7·33 „	7·40	— „

This substance melts at 181—182°, and is identical with ω-amidoethylpiperonylcarboxylic anhydride (p. 1013); it was, in fact, the first sample of this substance obtained.

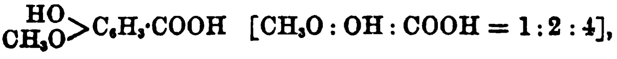
The dark brown alkaline solution which was separated from the crude substance $C_{10}H_9NO_3$, as described above, gave with hydrochloric acid a dark brown, amorphous precipitate. Boiling water dissolved the greater part of this precipitate, leaving a dark, resinous substance, which was separated by filtration. After treatment with animal charcoal, the hot aqueous solution deposited, on cooling, a light yellowish, crystalline powder, which, after repeated recrystallisation, became almost colourless, and gave the following numbers on analysis:—

0·1158 gram substance gave 0·0510 gram H_2O and 0·2430 gram CO_2.

	Theory. $C_8H_8O_4$.	Found.
C	57·14 per cent.	57·23 per cent.
H	4·76 „	4·89 „
O	38·09 „	37·88 „

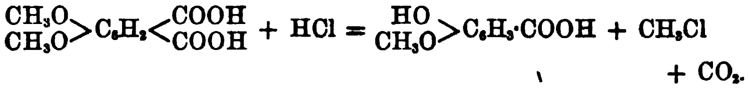
This acid melts at 245—247°, and when strongly heated in a stream of air, it gives a white, needle-shaped sublimate. It is readily soluble in hot water and alcohol, but sparingly so in the cold. The aqueous solution gives with ferric chloride a slight brownish coloration, and reduces ammoniacal nitrate of silver solution very readily. The acid dissolves in sulphuric acid, and on heating the solution to 100°, an intense green coloration is produced, which on standing becomes reddish-brown.

There can be no doubt that this substance is identical with isovanillic acid (methylprotocatechuic acid),



$$\genfrac{}{}{0pt}{}{HO}{CH_3O}\!>\!C_6H_3{\cdot}COOH \quad [CH_3O : OH : COOH = 1 : 2 : 4],$$

which Foster and Matthiessen (*Annalen*, Suppl. 2, 378) obtained by the action of hydrogen chloride on hemipinic acid.

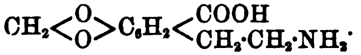


$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COOH\\COOH\end{matrix} + HCl = \begin{matrix}HO\\CH_3O\end{matrix}\!>C_6H_3\cdot COOH + CH_3Cl + CO_2.$$

Isovanillic acid melts at 250°, and has properties very similar to those described above.

At the high temperature employed, berberilic acid is evidently first split up into hemipinic acid and the anhydride $C_{10}H_9NO_3$ (see p. 1013); the hemipinic acid is then further decomposed by the steam evolved into isovanillic acid, carbon dioxide, and methyl alcohol, thus:—

$$C_{10}H_{10}O_6 + H_2O = C_8H_8O_4 + CH_3\cdot OH + CO_2.$$



Hydrolysis of Berberilic Acid. Preparation of ω-Amidoethylpiperonylcarboxylic Acid, $C_{10}H_{11}NO_4 = CH_2<\!\begin{matrix}O\\O\end{matrix}\!>C_6H_2<\!\begin{matrix}COOH\\CH_2\cdot CH_2\cdot NH_2\end{matrix}$.

Although anhydroberberilic acid is scarcely attacked by boiling dilute acids, berberilic acid is very readily decomposed by this treatment, with formation of hemipinic and amidoethylpiperonylcarboxylic acids, thus:—

$$C_{20}H_{19}NO_9 + H_2O = C_{10}H_{10}O_6 + C_{10}H_{11}NO_4.$$

This decomposition is best carried out as follows:—Anhydroberberilic acid, which should be as pure as possible, is dissolved in dilute potassium hydrate solution at 40°, the solution filtered, acidified, and the precipitated berberilic acid collected, washed, and ground up into a thin paste with water. 10 grams of this acid, in the form of paste, is mixed with 200 c.c. of 5 per cent. sulphuric acid, and the mixture vigorously boiled in a flask connected with a reflux apparatus. Decomposition sets in immediately, and in a short time the greater portion of the acid has passed into solution, giving place to a small quantity of a voluminous precipitate which floats in the liquid. The product is filtered, the precipitate washed well, dried on a porous plate, and recrystallised from acetic acid. The colourless, glistening needles thus obtained melt at 236°, and consist of pure anhydroberberilic acid. Analysis:—

0·1975 gram substance gave 0·0812 gram H_2O and 0·4332 gram CO_2.

	Theory. $C_{20}H_{17}NO_8$.	Found.
C........	60·15 per cent.	59·82 per cent.
H........	4·26 "	4·56 "

The amount of anhydroberberilic acid formed in this hydrolysis varies with the strength of the sulphuric acid employed. Under the above conditions, 10—15 per cent. of the berberilic acid is converted into anhydroberberilic acid, $C_{20}H_{17}NO_8$, whereas, if 50 per cent. sulphuric acid is used, as much as 50 per cent. of this acid is produced.

The acid solution containing the principal products of the reaction is evaporated to 100 c.c. and extracted at least 20, but better 30, times with small quantities of ether; the ethereal solution, which has a beautiful blue fluorescence, is washed with a little water, dried over calcium chloride, and evaporated, and the solid residue spread on a plate to remove traces of oily mother liquor. The crude hemipinic acid thus obtained may be purified by recrystallisation from water, but it is better to first convert the crude acid into its calcium salt and then to decompose this with hydrochloric acid. For this purpose, the crude acid is dissolved in warm water, neutralised with sodium hydrate, the solution filtered, cooled well, and mixed with a large excess of a strong solution of calcium chloride. The clear solution is then heated to boiling, the heavy, sandy precipitate of the calcium salt which forms, collected, washed with hot water, and dissolved in a small quantity of hot very dilute hydrochloric acid. This solution, on standing, deposits pure hemipinic acid in beautiful, lustrous prisms, which, after drying at 100°, gave the following results on analysis:—

I. 0·1430 gram substance gave 0·0595 gram H_2O and 0·2770 gram CO_2.

II. 0·1375 gram substance gave 0·0561 gram H_2O and 0·2678 gram CO_2.

	Theory. $C_{10}H_{10}O_6$.	Found. I.	II.
C	53·10 per cent.	52·82	53·12 per cent.
H	4·42 ,,	4·61	4·52 ,,
O	42·48 ,,	42·57	42·36 ,,

Allowing for regenerated anhydroberberilic acid, the amount of hemipinic acid obtained is very nearly theoretical.

During the extraction with ether, a quantity of a white precipitate generally separates, which consists of the sulphate of the new base $C_{10}H_{11}NO_4$; this is best removed by filtration from time to time, otherwise it is difficult to separate the ethereal and aqueous layers effectually. The acid liquors, which should be as free from hemipinic acid as possible, are carefully evaporated to about 50 c.c., care being taken to stop the evaporation as soon as any signs of charring are noticed. This solution, after standing for two days, deposits a large crop of beautifully-formed tabular crystals of the sulphate of the base

$C_{10}H_{11}NO_4$. These are collected, washed with a little water, dissolved in a small quantity of warm water, and barium hydrate solution carefully added until the sulphuric acid is *exactly* precipitated, care being taken that there is no excess of barium hydrate present in the liquid. The filtrate from the barium sulphate is evaporated at a gentle heat (70—80°) on a water-bath until sufficiently concentrated, and allowed to stand 24 hours, when a fine crop of slightly brownish, tabular crystals will have separated. These are collected, washed with a little water, and recrystallised from warm water. The air-dried crystals contain approximately one molecule of water of crystallisation, which is given off gradually over sulphuric acid in a vacuum, but much more readily at 100°, the crystals becoming quite opaque.

0·3141 gram substance, heated at 100° till constant, lost 0·0234 gram.

0·4384 gram substance, heated at 100° till constant, lost 0·0328 gram.

	Theory. $C_{10}H_{11}NO_4 + H_2O$.	Found. I.	II.
H_2O	7·93 per cent.	7·45	7·49 per cent.

The crystals, dried at 100°, gave the following results on analysis:—

I. 0·1598 gram substance gave 0·0802 gram H_2O and 0·3372 gram CO_2.

0·1087 gram substance gave 6·2 c.c. N; $t = 15°$; bar. = 738 mm.

II. 0·1060 gram substance gave 0·0542 gram H_2O and 0·2228 gram CO_2.

	Theory. $C_{10}H_{11}NO_4$.	Found. I.	II.
C	57·42 per cent.	57·54	57·32 per cent.
H	5·26 ,,	5·57	5·68 ,,
N	6·70 ,,	6·70	— ,,

This beautiful substance melts at 180—182° with evolution of gas. It is sparingly soluble in alcohol, benzene, acetone, and carbon bisulphide, readily soluble in hot water, moderately soluble in cold water.

On slowly cooling a moderately concentrated aqueous solution of the base, beautiful, tabular crystals gradually form. Professor Haushofer was kind enough to examine these for me, and has sent the following description:—

"The crystals of the base $C_{10}H_{11}NO_4$ belong to the *monoclinic* system, and represent the simple combination, 0P : ∞P. Owing to the predominance of the basal surface, the crystals have a tabular form. The following angles were measured:—

"∞P : ∞P (clinodiagonal prism face) .... 78° 53′

0P : ∞P (angle of the base and prism face) . . 101° 22′."

Salts of the Base $C_{10}H_{11}NO_4$.

This substance has very feeble acid properties, but, on the other hand, its basic properties are well marked, and it combines with acids, forming well-characterised salts.

The *sulphate*, $(C_{10}H_{11}NO_4)_2,H_2SO_4 + 2H_2O$, crystallises from water in beautiful, colourless prisms, readily soluble in hot, moderately so in cold, water. It melts at about 202—203° with decomposition. The water of crystallisation was determined in a sample of the salt which had stood for some days exposed to the air.

I. 0·9246 gram substance, heated at 100° till constant, lost 0·0592 gram.

II. 0·8680 gram substance, heated at 100° till constant, lost 0·0537 gram.

	Theory. $(C_{10}H_{11}NO_4)_2,H_2SO_4 + 2H_2O$.	Found. I.	Found. II.
H_2O	6·40 per cent.	6·29	6·19 per cent.

For analysis, the substance was dried at 100° until the weight was constant.

0·2050 gram substance dissolved in water and acidified with hydrochloric acid gave, on precipitation with barium chloride, 0·0942 gram $BaSO_4$.

0·1470 gram substance gave 0·0612 gram H_2O and 0·2514 gram CO_2.

	Theory. $(C_{10}H_{11}NO_4)_2,H_2SO_4$.	Found.
C	46·51 per cent.	46·64 per cent.
H	4·65 „	4·60 „
SO_4.......	18·60 „	18·93 „

The *hydrochloride*, $C_{10}H_{11}NO_4,HCl$, crystallises from water in colourless, microscopic needles, readily soluble in water, very sparingly in solutions containing much free hydrochloric acid.

The salt, dried over sulphuric acid, does not lose weight at 100°, and, therefore, contains no water of crystallisation. The following results were obtained on analysis:—

0·1376 gram substance gave 0·0621 gram H_2O, and 0·2450 gram CO_2.

0·5292 gram substance, dissolved in water, acidified with nitric acid, and precipitated with nitrate of silver, gave 0·3076 gram AgCl.

	Theory. $C_{10}H_{11}NO_4,HCl$.	Found.
C	48·90 per cent.	48·56 per cent.
H	4·89 „	5·02 „
Cl........	14·42 „	14·39 „

The Acid Oxalate, $C_{10}H_{11}NO_4,C_2H_2O_4$.—This beautiful salt is readily obtained by mixing a warm concentrated solution of the base with a considerable excess of oxalic acid and allowing the mixture to cool slowly. After standing for some time, long, pale-yellow needles make their appearance, and continue to grow until they almost fill the liquid. The crystals were collected, allowed to remain on a porous plate at the ordinary temperature for some days, and then analysed:—

0·1616 gram substance gave 0·2860 gram CO_2 and 0·0650 gram H_2O.

	Theory. $C_{10}H_{11}NO_4,C_2H_2O_4$.	Found.
C	48·16 per cent.	48·26 per cent.
H	4·35 „	4·47 „

It is readily soluble in hot water, moderately in cold water. It melts at about 202—203° with decomposition and rapid evolution of gas.

The Platinochloride, $(C_{10}H_{11}NO_4)_2,H_2PtCl_6$.—This was prepared by adding platinum chloride to the hot strong solution of the hydrochloride of the base, and allowing the solution to stand over night. The beautiful mass of light-reddish needles was collected, washed with water, recrystallised from this solvent, dried at 100°, and analysed.

I. 0·1940 gram substance gave 0·0557 gram H_2O, 0·2046 gram CO_2, and 0·0459 gram Pt.
II. 0·4568 gram substance gave 0·1074 gram platinum.
III. 0·3578 „ „ 0·0832 „
IV. 0·2291 „ „ 0·0542 „

	Theory. $(C_{10}H_{11}NO_4)_2,H_2PtCl_6$.	Found. I.	II.	III.	IV.	
C	29·00 p. c.	28·77	—	—	—	p. c.
H. ...	2·90 „	3·19	—	—	—	„
Pt	23·50 „	23·66	23·51	23·25	23·66	„

This salt crystallises from water in long, slender, straw-coloured needles, which, when rapidly heated in a capillary tube, became dark-coloured at about 200°, and melt with rapid decomposition at 222° with evolution of gas; when slowly heated, it becomes dark at 195—200°, and decomposes completely at about 212°.

The Aurochloride, $C_{10}H_{11}NO_4,HAuCl_4$.—This double salt is precipitated on the addition of gold chloride to a strong solution of the hydrochloride of the base as a light, chocolate-coloured, crystalline mass. It was dissolved in a little boiling water, filtered from a small quantity of a red, insoluble substance, and the solution allowed to stand for some hours. The crystalline precipitate which separated was collected, washed, dried at 100°, and analysed with the following result:—

0·3354 gram substance gave 0·1204 gram of gold.

	Theory. $C_{10}H_{11}NO_4,HAuCl_4$.	Found.
Au........	35·87 per cent.	35·89 per cent.

This salt thus obtained forms a chocolate-coloured, crystalline powder; which can be recrystallised from water, but not without slight decomposition.

Action of Heat on the Base $C_{10}H_{11}NO_4$.

In recrystallising this substance from boiling water, it was repeatedly noticed that if the boiling is continued for some time, decomposition takes place, and, instead of the thick, tabular plates of the original substance, thin, glittering plates were deposited as the solution cooled. These were collected, recrystallised from water, and analysed with the following results:—

0·1794 gram substance gave 0·0821 gram H_2O and 0·4125 gram CO_2.

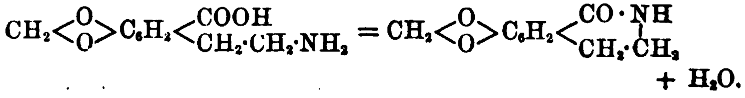
0·1623 gram substance gave 10·1 c.c. N; $t = 16°$; bar. = 740 mm.

	Theory. $C_{10}H_9NO_3$.	Found.
C........	62·82 per cent.	62·71 per cent.
H........	4·71 „	5·08 „
N........	7·33 „	7·30 „

This substance is identical with the anhydride $C_{10}H_9NO_3$ previously described (p. 1013).

The base $C_{10}H_{11}NO_4$ is also decomposed when heated for some little time at its melting point, and the residue, after recrystallisation from water, consists of the pure anhydride $C_{10}H_9NO_3$; it is therefore probable that the temperature 181—182°, given as the melting point of the base $C_{10}H_{11}NO_4$, is, more correctly, the temperature at which this substance is converted into the anhydride $C_{10}H_9NO_3$.

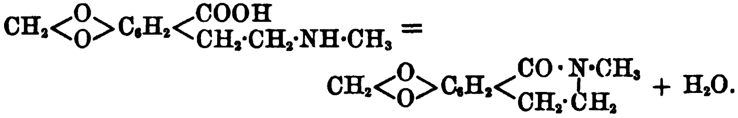
The explanation of this decomposition is that the compound $C_{10}H_{11}NO_4$, being both an acid and a base, on heating is converted into its inner anhydride, thus:—



$$CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}COOH\\CH_2\cdot CH_2\cdot NH_2\end{matrix} = CH_2{<}\begin{matrix}O\\O\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\cdot NH\\CH_2\cdot CH_2\end{matrix} + H_2O.$$

Action of Methyl Iodide on the Substance $C_{10}H_{11}NO_4$.

In assigning the correct constitution to this base, it was very important to obtain a methyl derivative which on heating would yield oxyhydrastinine, thus:—



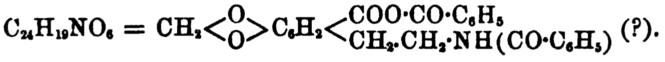
$$\mathrm{CH_2}\left<\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right>\mathrm{C_6H_2}\left<\begin{matrix}\mathrm{COOH}\\\mathrm{CH_2\cdot CH_2\cdot NH\cdot CH_3}\end{matrix}\right. = \mathrm{CH_2}\left<\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right>\mathrm{C_6H_2}\left<\begin{matrix}\mathrm{CO\cdot N\cdot CH_3}\\\mathrm{CH_2\cdot CH_2}\end{matrix}\right. + \mathrm{H_2O}.$$

With this object, the following experiments were instituted:—

1. The finely-divided base was dried at 100° and heated with a large excess of methyl iodide on a water-bath for two hours.
2. The pure, dry base was dissolved in methyl alcohol and heated in a sealed tube at 100° with excess of methyl iodide for one hour.
3. The base (1 mol.) was dissolved in methyl alcohol, a solution of potassium hydrate (1 mol.) in methyl alcohol added, and the whole heated with excess of methyl iodide at 100° for two hours.
4. Sodium ethylate was substituted for potassium hydrate in Experiment 3.

In no case could any methylated base be isolated, but in nearly every experiment an almost quantitative yield of the anhydride $C_{10}H_9NO_3$ was obtained. It is possible that the methylation of the base might take place at lower temperatures, but as the synthesis of oxyhydrastinine was accomplished in another way (p. 1034), these experiments were not continued.

Dibenzoylamidoethylpiperonylcarboxylic Acid,



$$\mathrm{C_{24}H_{19}NO_6} = \mathrm{CH_2}\left<\begin{matrix}\mathrm{O}\\\mathrm{O}\end{matrix}\right>\mathrm{C_6H_2}\left<\begin{matrix}\mathrm{COO\cdot CO\cdot C_6H_5}\\\mathrm{CH_2\cdot CH_2\cdot NH(CO\cdot C_6H_5)}\end{matrix}\right. (?).$$

As all attempts to prove the presence of an amido-group in the substance $C_{10}H_{11}NO_4$ by means of methyl iodide had failed, experiments were next tried on the action of benzoyl chloride on the base, and good results were obtained by using this reagent, together with sodium hydrate solution (Baumann's method). 2 grams of the pure base was dissolved in warm water, and 50 c.c. of 10 per cent. sodium hydrate solution and 7 grams of benzoyl chloride added alternately in small quantities at a time, the whole being well cooled during the operation. The reddish, resinous substance which separated was collected, washed with water, dissolved in boiling methyl alcohol, and the solution, after being concentrated considerably, allowed to stand 24 hours. At the end of this time, a quantity of almost colourless crystals had separated; these were collected, washed well with methyl alcohol, recrystallised from this solvent, and analysed with the following result:—

0·1492 gram substance gave 0·064 gram H_2O and 0·3781 gram CO_2.

0·1446 gram substance gave 4·3 c.c. nitrogen; $t = 14°$; bar. = 747 mm.

	Theory. $C_{24}H_{19}NO_6$.	Found.
C........	69·09 per cent.	69·10 per cent.
H........	4·56 „	4·79 „
N........	3·35 „	3·42 „

This beautiful substance melts at 148—150°, with slight previous softening. It is moderately soluble in hot alcohol, chloroform, and benzene, but only sparingly in these liquids in the cold, and almost insoluble in water and light petroleum. It is insoluble in aqueous hydrochloric acid and in ammonia in the cold, and seems to be only very slowly attacked by these reagents on boiling. This behaviour would seem to indicate that hydrogen atoms, both in the amido- and carboxyl-groups in the substance $C_{10}H_{11}NO_4$, had been replaced by benzoyl as shown in the formula assigned to this substance at the head of this section.

Action of Nitrous Acid on Amidoethylpiperonylcarboxylic Acid. Formation of Hydroxyethylpiperonylcarboxylic Acid (p. 1020).

In order to further confirm the formula assigned to the base $C_{10}H_{11}NO_4$, its behaviour towards nitrous acid was carefully studied.

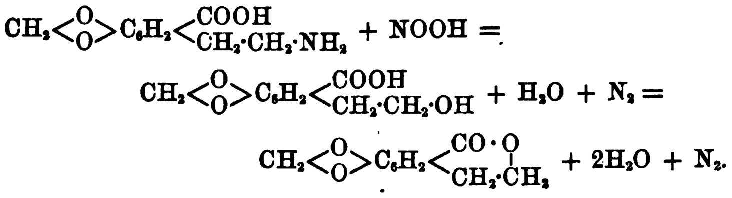
2 grams of the pure base was dissolved in 100 c.c. of warm water, 1 gram of pure sodium nitrite added, and then dilute hydrochloric acid (2 c.c. concentrated HCl and 10 c.c. water) gradually poured in, pieces of powdered ice being thrown in from time to time to prevent the temperature from rising. As the clear solution, even on standing, gave no precipitate, it was heated to boiling on a sand-bath for five minutes, and evaporated to about 50 c.c. Abundance of nitrogen and some nitrous acid were evolved during the decomposition, and on standing a crystalline precipitate separated, which was collected, washed with water, recrystallised from this solvent, and analysed with the following results:—

I. 0·1448 gram substance gave 0·0577 gram H_2O and 0·3310 gram CO_2.

II. 0·1619 gram substance gave 0·0638 gram H_2O and 0·3698 gram CO_2.

	Theory. $C_{10}H_8O_4$.		Found. I.	Found. II.	
C........	62·50	per cent.	62·34	62·79	per cent.
H........	4·16	,,	4·43	4·37	,,
O........	33·33	,,	32·23	32·84	,,

This substance melts at 126°, and is identical with *hydroxyethylpiperonylcarboxylic anhydride*, obtained by the action of potassium hydrate on the nitroso-compound, $C_{10}H_8N(NO)O_3$ (p. 1020). Its formation in the present instance is readily understood from the following equations:—



$$CH_2<\substack{O\\O}>C_6H_2<\substack{COOH\\CH_2\cdot CH_2\cdot NH_2} + NOOH =$$

$$CH_2<\substack{O\\O}>C_6H_2<\substack{COOH\\CH_2\cdot CH_2\cdot OH} + H_2O + N_2 =$$

$$CH_2<\substack{O\\O}>C_6H_2<\substack{CO\cdot O\\ |\\ CH_2\cdot CH_2} + 2H_2O + N_2.$$

The yield of the substance $C_{10}H_8O_4$ obtained in this reaction was good, but not quantitative.

Synthesis of Anhydroberberilic Acid.

As this substance is produced from berberilic acid by the action of heat, and as berberilic acid on hydrolysis yields hemipinic acid and the base $C_{10}H_{11}NO_4$, it was thought probable that by combining these two substances under suitable conditions a partial synthesis of anhydroberberilic acid might be accomplished.

With this object, the hemipinic salt of the base $C_{10}H_{11}NO_4$ was first prepared as follows:—1·2 grams of hemipinic acid, dissolved in 10 grams of water, was mixed with 1 gram of the base $C_{10}H_{11}NO_4$ (dissolved in 20 grams of water), the solution evaporated to a small bulk, and allowed to stand in a cold place. After 48 hours, a quantity of peculiar light yellow balls, grouped together in reniform masses, had separated. These were collected, washed with water, dried at 100°, and analysed with the following result:—

0·2798 gram substance gave 7·6 c.c. nitrogen; $t = 19°$; bar. = 750 mm.

	Theory. $C_{20}H_{21}NO_{10}$ $(C_{10}H_{11}NO_4\cdot C_{10}H_{10}O_6)$.	Found.
N........	3·10 per cent.	3·22 per cent.

This salt melts at about 155—160° with decomposition, becoming solid again almost at once. It is readily soluble in hot, moderately in cold water.

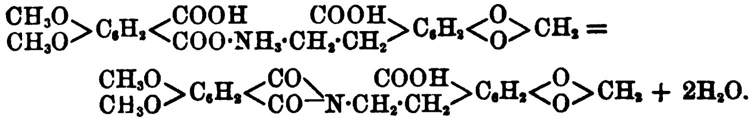
The pure, dry salt was now gradually heated to 180° in a wide test-tube in an oil-bath. Decomposition set in at about 160° with frothing and evolution of a quantity of water-vapour; this gradually subsided, and at the end of about 10 minutes the temperature was raised to 200° for a few minutes to complete the reaction. The resulting light brown oil, on cooling, solidified to a hard, transparent resin, which, however, when rubbed with a glass rod moistened with glacial acetic acid, soon became crystalline. The solid mass was ground up and dissolved in boiling 90 per cent. acetic acid, from which it separated on cooling in beautiful, glistening plates. These were collected, recrystallised from acetic acid, and analysed with the following result:—

0·1718 gram substance gave 0·0680 gram H_2O and 0·3786 gram CO_2.

0·2148 gram substance gave 6·3 c.c. nitrogen; $t = 18°$; bar. = 750 mm.

	Theory. $C_{20}H_{17}NO_8$.	Found.
C........	60·15 per cent.	60·10 per cent.
H........	4·26 „	4·39 „
N........	3·51 „	3·41 „

This beautiful substance melts at 236—237°, and is identical in every respect with the anhydroberberilic acid obtained by the oxidation of berberine, as described above (p. 1011). The formation by the above reaction is readily understood from the following equation:—

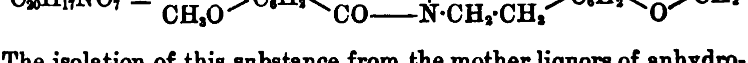


$$\begin{array}{l}CH_3O\\CH_3O\end{array}\!>C_6H_2<\!\begin{array}{l}COOH\qquad\quad COOH\\COO\cdot NH_3\cdot CH_2\cdot CH_2\end{array}\!>C_6H_2<\!\begin{array}{c}O\\O\end{array}\!>CH_2 =$$

$$\begin{array}{l}CH_3O\\CH_3O\end{array}\!>C_6H_2<\!\begin{array}{l}CO\diagdown\qquad COOH\\CO\!-\!N\cdot CH_2\cdot CH_2\end{array}\!>C_6H_2<\!\begin{array}{c}O\\O\end{array}\!>CH_2 + 2H_2O.$$

The yield of anhydroberberilic acid seemed to be nearly quantitative.

Berberal,



$$C_{20}H_{17}NO_7 = \begin{array}{l}CH_3O\\CH_3O\end{array}\!>C_6H_2<\!\begin{array}{l}COH\quad CO\text{———}\\CO\text{——}N\cdot CH_2\cdot CH_2\end{array}\!>C_6H_2<\!\begin{array}{c}O\\O\end{array}\!>CH_2.$$

The isolation of this substance from the mother liquors of anhydroberberilic acid, $C_{20}H_{17}NO_8$, by dilution with water, as explained in Part I of this research (p. 81), requires very carefully carrying out, as otherwise the crystals formed are so mixed up with tarry products that their subsequent purification is a matter of the utmost difficulty. In dealing with large quantities of these mother liquors, the bulk of the acetic acid was distilled off, the hot solution mixed with a very small quantity of boiling water, and allowed to stand for at least a week; the sides of the vessel containing it being scratched in several places with a glass rod. If no crystals had then formed, a small quantity more water was added, and the solution again allowed to stand, this treatment being repeated until the crystals deposited are so contaminated with tar that subsequent purification was almost impossible. In any case, a considerable quantity of the substance remains in the mother liquor. The yield varies with different preparations, but is rarely more than 10 grams from 1 kilo. of berberine hydrochloride.

A very pure sample of berberal was subjected to analysis with the following results:—

0·1433 gram substance gave 0·0590 gram H_2O and 0·3289 gram CO_2.

0·1995 gram substance gave 6·5 c.c. N; $t = 18·8°$; bar. = 760 mm.

	Theory. $C_{20}H_{17}NO_7$.	Found.	Mean of previous analyses.
C......	62·66 per cent.	62·53 per cent.	62·66 per cent.
H......	4·43 „	4·57 „	4·62 „
N......	3·66 „	3·76 „	3·77 „

The properties of berberal are given in detail in Part I of this research (p. 82).

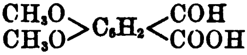
In the former paper (p. 83), it was mentioned that a solution of 0·7558 gram of berberal in 42·1296 grams of glacial acetic acid (m. p. 16·447°) was employed for the determination of the molecular weight of the substance by Raoult's method. This solution, on standing for 18 months, deposited long, colourless, transparent, prismatic needles; these were collected, washed with a little acetic acid, and drained on a porous plate. The crystals melted, not very sharply, at 115—120°. When heated at 105° for some hours, they became chalky, giving off acetic acid. The residual, very brittle mass melted at 148—150°, and gave, on analysis, the following numbers:—

0·2057 gram substance gave 6·8 c.c. N; $t = 15·5°$; bar. = 740 mm.

	Theory. $C_{20}H_{17}NO_7$.	Found.
N........	3·66 per cent.	3·72 per cent.

The substance was berberal, which, therefore, under certain conditions, crystallises with acetic acid in long, thin, transparent prisms.

Hydrolysis of Berberal. Preparation of Pseudopianic Acid,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COH\\COOH\end{matrix}\ [CH_3O:CH_3O:COH:COOH = 1:2:3:4].$$

The most important property of berberal, and the property which affords the best clue to its constitution, is the decomposition which it undergoes when boiled with dilute sulphuric acid, when it is split up into pseudopianic acid and amidoethylpiperonylcarboxylic anhydride (p. 1013), thus:—

$$C_{20}H_{17}NO_7 + H_2O = C_{10}H_{10}O_5 + C_{10}H_9NO_3.$$

In carrying out this hydrolysis, the very finely-divided pure substance is transferred to a flask connected with a reflux apparatus and boiled briskly with an excess of dilute sulphuric acid (25 per cent.), the whole being vigorously shaken from time to time. In the course of about half an hour, the greater part of the substance dissolves, forming a deep reddish-brown solution, in which a small quantity of a tarry matter swims about. This tarry substance, which completely solidifies on cooling, is collected, washed with water, and recrystallised from alcohol. When analysed, it gave the following result:—

0·1440 gram substance gave 0·0607 gram H_2O and 0·3302 gram CO_2.

	Theory. $C_{20}H_{17}NO_7$.	Found.
C........	62·66 per cent.	62·53 per cent.
H........	4·43 „	4·68 „

It melts at 149°, and consists of unchanged berberal.

The conditions in the experiments on the hydrolysis of berberal were very considerably varied, but in every instance similar tarry substances were formed which did not become appreciably less even after six hours' boiling. It is probable that the small quantity of tar always produced coats a certain portion of the berberal, and thus prevents it from coming in contact with the acid; and, indeed, unless the berberal employed be very pure and in a very fine state of division, it is scarcely attacked by boiling dilute sulphuric acid.

The products of the hydrolysis were isolated as follows:—

The acid liquor was evaporated to about three-fourths of its bulk, extracted 20 times with ether, the ethereal solution washed with a little water, and evaporated. The yellowish-white crystalline residue, which contains two substances, was boiled with a little very dilute sodium carbonate solution, until completely dissolved, and the alkaline liquid filtered and allowed to stand in a cold place for some hours. The crystals which separated were collected, washed with a little water, and recrystallised from this solvent.

They then melted at 182°, and were found to consist of the pure amidoethylpiperonylcarboxylic anhydride $C_{10}H_9NO_3$ (p. 1013).

Analysis:—

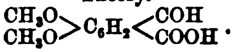
0·1153 gram substance gave 0·0536 gram H_2O and 0·2650 gram CO_2.

	Theory. $C_{10}H_9NO_3$.	Found.
C........	62·82 per cent.	62·68 per cent.
H........	4·71 ,,	5·16 ,,

As the anhydride $C_{10}H_9NO_3$ is only sparingly soluble in ether, the amount extracted in this way is small, and the bulk of the substance remains behind in the sulphuric acid liquors. To recover it, the liquors are boiled with excess of barium carbonate, filtered hot, and evaporated to a small bulk; the solution, on cooling, deposits a quantity of crystals of almost pure anhydride, $C_{10}H_9NO_3$.

The alkaline solution from which the small quantity of the anhydride, $C_{10}H_9NO_3$, had crystallised, as described above, was evaporated to half its bulk, cooled well, filtered from a small quantity of the anhydride which separated, and acidified with hydrochloric acid. The beautifully white, crystalline mass which separated was collected, washed with water, and purified by repeated recrystallisation from this solvent. An analysis of a portion of the substance, dried at 100°, gave the following numbers:—

0·1591 gram substance gave 0·0722 gram H_2O and 0·3332 gram CO_2.

	Theory.  $\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COH\\COOH\end{matrix}$.	Found.
C........	57·14 per cent.	57·13 per cent.
H........	4·76 ,,	5·04 ,,
O........	38·09 ,,	37·83 ,,

Pseudopianic acid melts at 121—122°. It is readily soluble in hot water, alcohol, acetone, benzene, and chloroform, sparingly in cold water and light petroleum. It crystallises from hot water in long, slender needles, grouped together to a wool-like mass; from benzene it crystallises in slender needles, and from chloroform in long, flat needles. In its appearance and properties it bears considerable resemblance to opianic acid. When warmed with phenol and much sulphuric acid, a green solution is formed, which, on further heating, becomes violet-brown; the addition of an equal bulk of water to this produces a beautiful violet solution, which, on the careful addition of alkali, turns first a brilliant blue and finally green. (Compare the Formation of Opiaurin from Opianic Acid. Liebermann and Seidler, *Ber.*, 20, 873.)

Fusion of Pseudopianic Acid with Potassium Hydrate.—A small quantity of the acid was dissolved in a strong solution of potassium hydrate, the liquid evaporated in a silver dish, and the residue gently fused at about 180—200°. The residue was dissolved in water, acidified with dilute sulphuric acid, and repeatedly extracted with ether. The ethereal solution, on evaporation, deposited a thick, pale-brown syrup, from which, on standing, a small quantity of a crystalline substance separated. The solution of the latter in water gave, with ferric chloride, an intense green coloration, becoming violet, and ultimately red, on the addition of sodium bicarbonate; it also reduced Fehling's solution and ammoniacal nitrate of silver in the cold.

This experiment shows that pseudopianic acid is a catechol derivative.

Estimation of the Methoxyl Groups in Pseudopianic Acid by Zeisel's Method.—The previous experiment showed that pseudopianic acid contains two hydroxyl groups in the ortho-position; but as the acid itself gives no coloration with ferric chloride, it follows that these must be present, either as two methoxy-groups (CH_3O) or as a methylene dioxy-group ($CH_2{<}^{O}_{O}$). In order to decide this point the action of fuming hydriodic acid on the acid was investigated; the apparatus described by Zeisel (*Monatsh.*, 6, 995) being employed for the purpose.

0·3726 gram substance was heated with a large amount of fuming hydriodic acid (sp. gr. 1·96), and the escaping methyl iodide, led into an alcoholic solution of silver nitrate, gave 0·8164 gram AgI.

	Theory for 2(OCH_3) groups in $C_{10}H_{10}O_5$.	Found.
(OCH_3)...	29·5 per cent.	28·9 per cent.

Pseudopianic acid, therefore, contains two methoxy-groups in the ortho-position.

Basicity of Pseudopianic Acid.—In order to determine the basicity of this acid, a weighed quantity was dissolved in water and titrated with a standard solution of potassium hydrate, with the result that the acid was shown to be *monobasic.*

0·8432 gram substance required for neutralisation 41·3 c.c. of potassium hydrate solution, 1 c.c. of which contained 0·005461 gram KOH.

This corresponds with 0·2256 gram KOH, and agrees closely with the amount required for a monobasic acid, that is, 0·2249 gram.

Salts of Pseudopianic Acid.—In order to prepare the salts of this acid, the pure substance was dissolved in hot water, a slight excess of ammonia added, and the solution allowed to stand over sulphuric acid until quite neutral. On adding silver nitrate to this neutral solution, a white, crystalline precipitate of the *silver salt*, $C_{10}H_9O_5Ag$, was formed. This was collected, well washed with water, dried on a porous plate over sulphuric acid in a vacuum, and analysed with the following result:—

0·1960 gram substance gave 0·0569 gram H_2O, 0·2709 gram CO_2, and 0·0662 gram Ag.

	Theory. $C_{10}H_9O_5Ag$.	Found.
C	37·85 per cent.	37·70 per cent.
H........	2·84 ,,	3·22 ,,
Ag	34·07 ,,	33·77 ,,

This salt, when examined under the microscope, is seen to consist of slender needles; these are moderately readily soluble in hot water, and when heated in a capillary tube decompose at about 195° with blackening.

A dilute neutral solution of the ammonium salt shows the following behaviour with reagents:—

Copper Sulphate.—A pale green, amorphous precipitate, especially on warming.

Lead Acetate.—A white, amorphous precipitate, soluble in hot water.

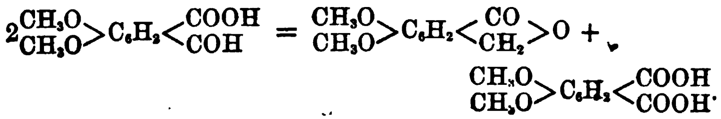
Zinc Sulphate.—A white, amorphous precipitate, more readily produced in warm solutions.

Calcium Chloride and *Barium Chloride.*—No precipitate.

The *potassium salt* of pseudopianic acid separates from its concentrated solution in long, transparent needles, on the addition of strong potassium hydrate solution (sp. gr. 1·4). It is very readily soluble in water.

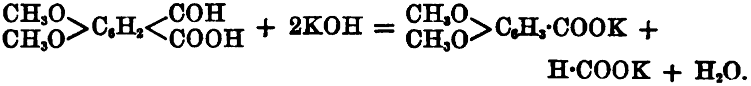
Action of Potassium Hydrate on Pseudopianic Acid. Formation of Veratric Acid, $(CH_3O)_2C_6H_3{\cdot}COOH\ [CH_3O : CH_3O : COOH = 1 : 2 : 4]$.

According to Matthiessen and Forster (*Annalen*, Suppl. 1, 332), opianic acid is decomposed by boiling concentrated potassium hydrate into meconine and hemipinic acid, thus:—



$$2\begin{matrix}\mathrm{CH_3O}\\\mathrm{CH_3O}\end{matrix}\!>\mathrm{C_6H_2}<\!\begin{matrix}\mathrm{COOH}\\\mathrm{COH}\end{matrix} = \begin{matrix}\mathrm{CH_3O}\\\mathrm{CH_3O}\end{matrix}\!>\mathrm{C_6H_2}<\!\begin{matrix}\mathrm{CO}\\\mathrm{CH_2}\end{matrix}\!>\mathrm{O} + \begin{matrix}\mathrm{CH_3O}\\\mathrm{CH_3O}\end{matrix}\!>\mathrm{C_6H_2}<\!\begin{matrix}\mathrm{COOH}\\\mathrm{COOH}\end{matrix}.$$

Pseudopianic acid, when similarly treated, is acted on quite differently, the products of its decomposition being veratric and formic (?) acids, thus :—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COH\\COOH\end{matrix} + 2KOH = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_3{\cdot}COOK + H{\cdot}COOK + H_2O.$$

In studying this decomposition, the acid was dissolved in a little dilute potassium hydrate, an excess of a concentrated solution of potassium hydrate (sp. gr. 1·4) added, and the whole boiled for one hour. The potassium salt of pseudopianic acid, which first separates out, dissolves readily on warming, and the solution, although it remains quite clear, becomes slightly yellow as the reaction proceeds. The product was diluted with a considerable quantity of water, acidified with hydrochloric acid, and extracted ten times with pure ether. The ethereal solution, after washing with a little water and drying over calcium chloride, deposited, on evaporation, a yellowish, crystalline residue, which, after repeated recrystallisation from hot water, was obtained pure, in the form of colourless needles.

Analysis :—

0·1308 gram substance gave 0·0640 gram H_2O and 0·2855 gram CO_2.

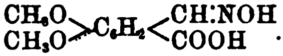
	Theory. $C_9H_{10}O_4$.	Found.
C........	59·34 per cent.	59·53 per cent.
H........	5·49 ,,	5·44 ,,
O........	35·17 ,,	35·03 ,,

The acid melts at 176—178°. It is readily soluble in hot, but only sparingly in cold water; the hot solution, on cooling, deposits the substance in slender needles. It is also readily soluble in alcohol and ether, and its aqueous solution gives no coloration with ferric chloride. From the results of the analysis and the study of the properties of this substance, there can scarcely be a doubt that it is veratric acid, which melts at 179·5°.

In order, however, to be certain of the identity of the two substances, the acid from pseudopianic acid was converted into the voluminous, crystalline silver salt, and this, after careful drying, digested for half an hour with methyl iodide and a quantity of pure ether. The ethereal solution was filtered from the precipitated silver iodide, evaporated, and the residual, colourless, crystalline mass purified by repeated recrystallisation from a mixture of benzene and light petroleum. In this way, the methyl salt was obtained in the form of colourless needles melting at 58—59°; this corresponds exactly with the melting point of methyl veratrate. Unfortunately the amount of methyl salt obtained was too small for analysis; but a direct comparison of the acid and its methyl salt with veratric acid and its methyl salt left no doubt as to the identity of the two preparations.

According to the equation at the head of this chapter, which is supposed to represent the action of potassium hydrate on pseudopianic acid, formic acid should be produced. In order to test this, the acid liquors from which the veratric acid had been extracted by ether, as explained above, were distilled in steam. The distillate had a distinctly acid reaction and slight reducing powers, but the quantity of formic acid, which in any case could have been present, was so small, that this test can scarcely be looked on as satisfactory.

Oxime of Pseudopianic Acid,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CH{:}NOH\\COOH\end{matrix}.$$

In order to prepare this interesting substance, 1 gram of the pure acid was dissolved in dilute potassium hydrate solution (containing 3 grams of KOH), a solution of 1 gram of hydroxylamine hydrochloride in a little water added, and the whole allowed to stand for 24 hours. The product was rendered slightly acid with hydrochloric acid, the white, sandy precipitate which separated collected, washed well, and dried on a porous plate over sulphuric acid in a vacuum. It gave the following results on analysis:—

0·1842 gram substance gave 0·0880 gram H_2O and 0·3577 gram CO_2.

0·1997 gram substance gave 11·2 c.c. N; $t = 20°$; bar. = 740 mm.

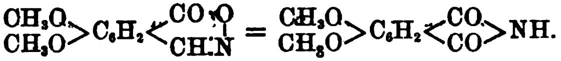
	Theory. $C_{10}H_{11}NO_5$.	Found.
C........	53·33 per cent.	52·91 per cent.
H........	4·88 ,,	5·30 ,,
N........	6·22 ,,	6·20 ,,

Pseudopianic oxime melts approximately at 124°, but its melting point could not be accurately determined, owing to the fact that the substance decomposes entirely at about 120° with evolution of gas, and it then becomes quite solid, but melts again at about 215°. The study of this decomposition is given in the next section. Pseudopianic oxime crystallises from water in little balls of needles. It is readily soluble in alkalis and alkaline carbonates, also in hot water and alcohol, but only sparingly so in benzene, chloroform, and light petroleum.

Action of Heat on the Oxime of Pseudopianic Acid.

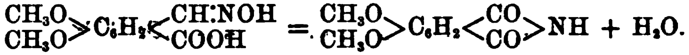
Formation of Hemipinimide, $\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\\CO\end{matrix}>NH$.

The anhydride of the oxime of opianic acid, when heated slightly above its melting point (115°), undergoes a very remarkable molecular change, and is converted into hemipinimide (Liebermann, *Ber.*, **19**, 2924).



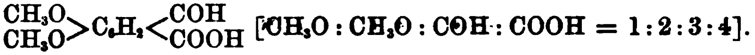
$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\cdot O\\CH:N\end{matrix} = \begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\\CO\end{matrix}>NH.$$

As already stated, the oxime of pseudopianic acid is decomposed at its melting point, and on studying this reaction it was found that in this case also hemipinimide is formed, thus:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CH:NOH\\COOH\end{matrix} = \begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\\CO\end{matrix}>NH + H_2O.$$

This very important fact proves conclusively that pseudopianic acid has the constitution



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COH\\COOH\end{matrix} [CH_3O : CH_3O : COH : COOH = 1:2:3:4].$$

The conversion of the oxime of pseudopianic acid into hemipinimide may be accomplished in a variety of ways, as, for instance, by boiling with dilute hydrochloric acid; but the simplest method is to heat the substance for about 10 minutes in a test-tube at 160—180°. The crystals first melt, then water vapour is given off, and the whole finally solidifies to a hard, crystalline cake. This is ground up, dissolved in the least quantity of boiling alcohol (it is but very sparingly soluble in this solvent), filtered, and the solution allowed to stand. In a short time needle-shaped crystals separate, which consist of pure hemipinimide.

Analysis:—

0·1856 gram substance gave 11·2 c.c. of nitrogen; $t = 23$; bar. = 755.

	Theory. $C_{10}H_9NO_4$.	Found.
N........	6·77 per cent.	6·78 per cent.

The substance melted at 224—226°, and showed all the properties of hemipinimide.

Oxime of Opianic Acid, $\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COOH\\CH:NOH\end{matrix}$.

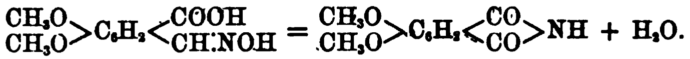
Liebermann (*Berichte*, **19**, 2923) found that when opianic acid or its ethyl salt is treated in alcoholic solution with hydroxylamine hydrochloride in the cold, a substance, $C_{10}H_9NO_4$ (opianoxime anhydride), is formed, which would seem to be the inner anhydride of the oxime of opianic acid, $C_{10}H_{11}NO_5$, and he thus seems to draw the conclusion from his experiments that the oxime itself is not capable of existence. This substance may, however, be readily prepared in the following way:—The pure acid (1 mol.) is dissolved in a dilute solution of potassium hydrate (4 mols.), mixed with hydroxylamine hydrochloride (1½ mols.), and left for 12 hours. If the clear solution is then acidified and allowed to stand, long, slender, needle-shaped crystals separate; these are collected, well washed with water, and dried for some days on a porous plate at the ordinary temperature and then for a few minutes at 50°. This substance is the oxime of opianic acid, as is apparent from the following analytical results:—

0·1630 gram substance gave 0·0738 gram H_2O and 0·3227 gram CO_2.

0·1504 gram substance gave 8·0 c.c. nitrogen; $t = 14°$; bar. = 740 mm.

	Theory. $C_{10}H_{11}NO_5$.	Found.
C........	53·33 per cent.	53·37 per cent.
H........	4·88 ,,	5·03 ,,
N........	6·22 ,,	6·09 ,,

The oxime of opianic acid melts at about 82—83°, but the melting point varies considerably with the rapidity with which the heating is conducted; on further rapid heating, it remains liquid till about 130°, when it suddenly becomes solid, owing to formation of hemipinimide, thus:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}COOH\\CH{:}NOH\end{matrix} = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}CO\\CO\end{matrix}\!>\!NH + H_2O.$$

This remarkable isomeric change takes place sometimes at much lower temperatures; thus, if the oxime is heated at 80°, after some time the whole becomes converted into a solid cake of hemipinimide. This change is accompanied by the evolution of a very considerable amount of heat (compare Liebermann, *Ber.*, **19**, 2924), and in one case, when an ethereal solution of about 10 grams of the oxime was evaporated on a water-bath, the temperature rose so rapidly as to crack the flask in several places.

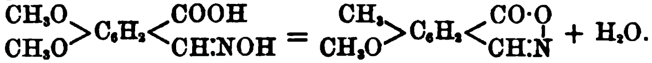
The oxime of opianic acid is extremely soluble in alcohol, readily in ether, hot chloroform, and benzene, but only sparingly in light petroleum and carbon bisulphide. It is very readily soluble in warm water, moderately in cold water; the hot solution, on cooling, deposits the substance in needles.

If, however, the aqueous solution is boiled for a short time, decomposition into water and opianoxime anhydride takes place, and on cooling, this anhydride separates in small, colourless, needle-shaped crystals. These, after recrystallisation, and drying, for some days at the ordinary temperature and then for a few minutes at 40—50°, gave the following results on analysis:—

0·1739 gram substance gave 0·0720 gram H_2O and 0·3667 gram CO_2.

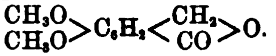
	Theory. $C_{10}H_9O_4$.	Found.
C........	57·97 per cent.	57·51 per cent.
H........	4·34 „	4·60 „

This substance showed all the properties ascribed to opianoxime-anhydride by Liebermann (*Ber.*, 19, 2923). The crystals melted apparently at 112—115°, but the mass solidified again at once, owing to its being converted into hemipinimide. This decomposition of the oxime of opiamic acid into its anhydride is probably represented by the equation



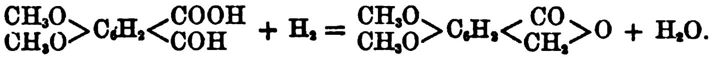
$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COOH\\CH{:}NOH\end{matrix} = \begin{matrix}CH_3\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CO\cdot O\\CH{:}N\end{matrix} + H_2O.$$

Reduction of Pseudopianic Acid. Formation of Pseudomeconine,



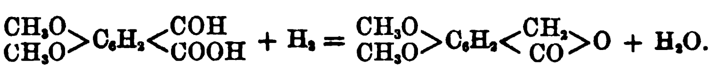
$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CH_2\\CO\end{matrix}\!>O.$$

Opianic acid is readily reduced by sodium amalgam with formation of meconine (Matthiessen, Foster, *Chem. Soc. J.*, 1863, 446):—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COOH\\COH\end{matrix} + H_2 = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CO\\CH_2\end{matrix}\!>O + H_2O.$$

Pseudopianic acid under the same treatment yields pseudomeconine, thus:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COH\\COOH\end{matrix} + H_2 = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CH_2\\CO\end{matrix}\!>O + H_2O.$$

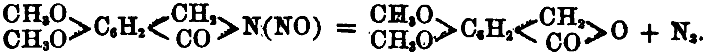
1 gram of the pure acid was dissolved in a dilute solution of sodium carbonate, and then 50 grams of 2½ per cent. sodium amalgam gradually added. After standing for 24 hours, the aqueous layer was poured off the mercury, nearly neutralised, filtered, and acidified with hydrochloric acid. The white, crystalline precipitate which separated was collected, washed with water, and recrystallised from this solvent. The crystals obtained melted between 117° and 122°, and were therefore not quite pure; they were dissolved in hot water, the solution cooled until the substance just commenced to crystallise out, two or

three drops of sodium carbonate solution added, and the whole allowed to stand until quite cold. The resulting colourless needles were collected, washed with water, dried at 100°, and analysed with the following result:—

0·1525 gram substance gave 0·0716 gram H_2O and 0·3450 gram CO_2.

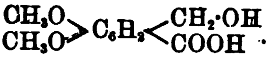
	Theory. $C_{10}H_{10}O_4$.	Found.
C........	61·85 per cent.	61·69 per cent.
H........	5·16 „	5·22 „
O........	32·99 „	33·09 „

This substance melts at 123—124°, and is in all its properties identical with pseudomeconine, which Salomon (*Ber.*, **20**, 884) obtained by boiling nitrosohemipinimidine with sodium hydrate:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CH_2\\CO\end{matrix}\!>N(NO) = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CH_2\\CO\end{matrix}\!>O + N_2.$$

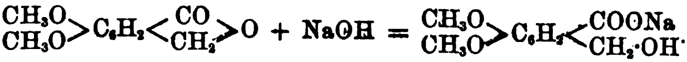
Pseudomeconinic Acid,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CH_2{\cdot}OH\\COOH\end{matrix}.$$

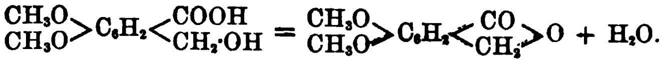
In experimenting with meconine and pseudomeconine, it was found that although they are very similar in their general reactions, yet they differ widely in the following respect:—

Meconine dissolves readily in dilute sodium hydrate solution with formation of the sodium salt of meconinic acid:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CO\\CH_2\end{matrix}\!>O + NaOH = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COONa\\CH_2{\cdot}OH\end{matrix}.$$

On the addition of acids, the free meconinic acid is at once split up into its anhydride, meconine, and water thus:—

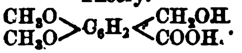


$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COOH\\CH_2{\cdot}OH\end{matrix} = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CO\\CH_2\end{matrix}\!>O + H_2O.$$

Pseudomeconine is also readily soluble in alkalis, with formation of a salt of pseudomeconinic acid, and on acidifying, the free acid, which is much more stable than meconinic acid, does not decompose, but gradually separates in a pure condition in the form of long, slender, colourless needles. A quantity of this beautiful acid was prepared, washed with water, dried at the ordinary temperature for some days, and then at 40—50° for some minutes, and analysed with the following results:—

0·1446 gram substance gave 0·0728 gram H_2O and 0·3007 gram CO_2.

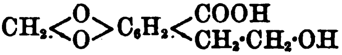
Theory.



$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CH_2OH\\COOH.\end{matrix}$

	Theory.	Found.
C........	56·60 per cent.	56·71 per cent.
H........	5·66 „	5·60 „
O..........	37·73 „	37·69 „

Pseudomeconinic acid is very readily converted into pseudomeconine on heating, and it therefore shows practically the same melting point as the latter, the melting of the substance in this case being, however, accompanied by evolution of bubbles of gas (steam). It is much more soluble in water and in most other solvents than pseudomeconine, and differs from its anhydride in the fact that it dissolves readily in a solution of sodium carbonate in the cold. When boiled with water, pseudomeconinic acid dissolves, and, on cooling, beautiful needle-shaped crystals of pseudomeconine separate. In this respect, and in its general behaviour, this acid shows a great similarity to ω-hydroxyethylpiperonylcarboxylic acid,



$$CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}COOH\\CH_2{\cdot}CH_2{\cdot}OH\end{matrix}$$ (p. 1020).

The wide difference in tendency to form inner anhydrides exhibited by two such closely allied substances as meconinic acid and pseudomeconinic acid is very interesting, and experiments are in progress with a view to obtaining further evidence which may throw light on this point.

Salts of Pseudomeconinic Acid.—Pseudomeconinic acid is a strong monobasic acid, as the following experiments show:—

0·3477 gram of the pure acid was dissolved in an excess of standard KOH solution, and the excess titrated back with standard sulphuric acid, using phenolphthaleïn as an indicator. It was found that this amount of substance required for neutralisation 0·0987 gram KOH, whereas on the assumption that a salt, $C_{10}H_{11}O_5K$, had been formed, 0·0915 gram of KOH is required.

Silver Pseudomeconinate, $C_{10}H_{11}O_5Ag$.—To prepare this salt, the pure acid was dissolved in a slight excess of a dilute solution of ammonia, the excess of ammonia allowed to evaporate over sulphuric acid in a vacuum, and the neutral solution precipitated with nitrate of silver. A white, curdy precipitate was obtained, which rapidly became crystalline. It is readily soluble in hot water, and crystallises on cooling in long, slender needles.

Analysis:—

I. 0·1724 gram substance gave 0·0539 gram H_2O, 0·2370 gram CO_2, and 0·0583 gram Ag.

II. 0·4372 gram substance gave 0·1484 gram Ag.

	Theory. $C_{10}H_{11}O_5Ag$.		Found. I.	Found. II.	
C........	37·66	per cent.	37·49	—	per cent.
H........	3·45	,,	3·48	—	,,
Ag......	33·77	,,	33·89	33·94	,,

The neutral solution of the ammonium salt gives no precipitatate with lead acetate, barium chloride, or zinc sulphate; a bright green precipitate is produced on the addition of copper sulphate.

Action of Alkalis on Berberal.

Formation of Pseudopianic Acid, $C_{10}H_{10}O_5$; *Pseudopianate of ω-Amidoethylpiperonylcarboxylic Anhydride*, $C_{20}H_{19}NO_8$; *and of ω-Amidoethylpiperonylcarboxylic Anhydride*, $C_{10}H_9NO_3$.

Berberal is insoluble in aqueous alkalis and in alkaline carbonates, but when treated with alcoholic potash, it is readily decomposed, and on the addition of an acid, the above three substances are obtained, the study of which has afforded a clear insight into the constitution of berberal.

In carrying out this hydrolysis, finely powdered berberal is mixed into a thin paste with a little methyl alcohol, heated just to boiling, and then methyl alcoholic potash added drop by drop until the substance has just dissolved, and a drop of the solution mixed with warm water gives only a very slight precipitate. Water is now added, the solution boiled until free from alcohol, acidified with dilute hydrochloric acid, and allowed to stand in a cool place for an hour. A new substance is thus obtained in colourless needles, which, after recrystallisation from water and drying at 100°, gave the following numbers on analysis:—

I. 0·1114 gram substance gave 0·0542 gram H_2O and 0·2438 gram CO_2.

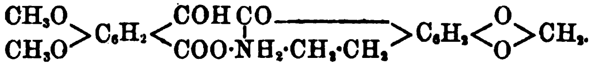
0·1180 gram substance gave 3·7 c.c. nitrogen; $t = 18°$; bar. = 725 mm.

II. 0·1540 gram substance gave 0·0714 gram H_2O and 0·3380 gram CO_2.

III. 0·1069 gram substance gave 0·0488 gram H_2O and 0·2336 gram CO_2.

	Theory. $C_{20}H_{19}NO_8$.		Found. I.	Found. II.	Found. III.	
C......	59·85	per cent.	59·58	59·85	59·69	per cent.
H......	4·74	,,	5·20	5·04	5·07	,,
N......	3·49	,,	3·58	—	—	,,

This new substance is the *pseudopianate* of *ω-amidoethylpiperonylcarboxylic anhydride* (p. 1080), and has the constitution



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COH\ CO\text{————————}\\COO\cdot NH_2\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2.$$

It melts at 149°, and as this temperature corresponds very closely with that noticed as the melting point of berberal (149—150°), it is probable that at this temperature the substance $C_{20}H_{19}NO_8$ is converted into berberal with elimination of water, thus:—

$$C_{20}H_{19}NO_8 = C_{20}H_{17}NO_7 + H_2O,$$

a change which certainly takes place at higher temperatures (p. 1081). The substance $C_{20}H_{19}NO_8$ is readily soluble in boiling water, but only sparingly in cold; the hot solution, on cooling, deposits the substance in the form of slender, colourless needles. It is also readily soluble in methyl and ethyl alcohol and benzene, but only sparingly in light petroleum or carbon bisulphide.

The substance $C_{20}H_{19}NO_8$ is very readily decomposed by alkalis and alkaline carbonates, with formation of pseudopianic acid and ω-amidoethylpiperonylcarboxylic anhydride, thus:—

$$C_{20}H_{19}NO_8 + KOH = C_{10}H_9O_5K + C_{10}H_9NO_3 + H_2O.$$

In studying this decomposition, the finely divided substance was mixed with dilute ammonia solution, warmed gently, and shaken vigorously. A considerable portion dissolved, but in a short time a white, crystalline precipitate settled out. This was collected, washed with water, recrystallised from this solvent, and analysed with the following result:—

0·1204 gram substance gave 0·0540 gram H_2O and 0·2778 gram CO_2.

	Theory. $C_{10}H_9NO_3$.	Found.
C........	62·83 per cent.	62·92 per cent.
H........	4·71 „	4·98 „

It melts at 181°, and is identical with *ω-amidoethylpiperonylcarboxylic anhydride* (p. 1013).

The filtrate from this substance was boiled on a reflux apparatus for about half an hour, and allowed to stand over night, when an almost colourless, crystalline substance separated, which after recrystallisation from alcohol melted at 149—150°, and showed all the properties of berberal.

The clear alkaline liquid was acidified with hydrochloric acid, and the crystalline precipitate which formed collected, washed with water, and recrystallised from this solvent. In this way, thin, colourless needles were obtained, which were dried at 100°, and analysed with the following result:—

0·1060 gram substance gave 0·0484 gram H_2O and 0·2219 gram CO_2.

	Theory. $C_{10}H_{10}O_5$.	Found.
C........	57·14 per cent.	57·09 per cent.
H........	4·76 „	5·07 „
O........	38·09 „	37·84 „

This acid melts at 119—120°, and is identical with pseudopianic acid, $\begin{matrix}CH_3O\\CH_3O\end{matrix}{>}C_6H_2{<}\begin{matrix}COH\\COOH\end{matrix}$, the properties of which are given in detail on p. 1065.

Dilute acids appear to decompose the substance $C_{20}H_{19}NO_8$ with almost as great ease as alkalis. A few crystals of it, boiled in a test-tube with a little 10 per cent. sulphuric acid, rapidly dissolved, and on cooling crystals separated which, after recrystallisation from water, were readily identified as the anhydride $C_{10}H_9NO_3$. Ether extracted from the acid liquor a white, crystalline acid, which showed all the properties of pseudopianic acid. The substance $C_{20}H_{19}NO_8$ is, however, perfectly stable in neutral solutions, and may be recrystallised several times from water without seeming to undergo the least decomposition.

Action of Phenylhydrazine on Berberal.

In order to obtain some further clue to the constitution of berberal, a number of experiments on the behaviour of this substance towards reagents, and especially towards phenylhydrazine, were instituted; but although the conditions of the experiment were varied as much as possible, no definite compound of the two substances could be isolated with certainty.

The following experiment, however, gave interesting results:—2 grams of berberal, 5 grams of phenylhydrazine hydrochloride, 15 grams of crystallised sodium acetate, and about 100 c. c. of 70 per cent. alcohol were heated together in a sealed tube at 130° for four hours. The resulting slightly yellowish solution was transferred to a dish, mixed with water, and gently heated on a water-bath, until all the alcohol had evaporated. During this operation, a reddish-brown, flocculent substance separated, which was collected, washed well with water, and ground up in a mortar with a little methyl alcohol. This treatment removed a sticky, resinous substance, leaving an almost colourless powder, very insoluble in the usual solvents. It was ultimately purified by repeated recrystallisation from isoamyl alcohol, the crystals well washed, first with isoamyl alcohol, then with methyl alcohol, and dried at 100°.

The analysis gave the following numbers:—

I. 0·1488 gram substance gave 0·0812 gram H_2O and 0·3710 gram CO_2.

0·2052 gram substance gave 25·2 c.c. N; $t = 15°$; bar. = 753 mm.

II. 0·1483 gram substance gave 0·0786 gram H_2O and 0·3684 gram CO_2.

0·2404 gram substance gave 29·5 c.c. N; $t = 17°$; bar. = 756 mm.

III. 0·1654 gram substance gave 0·0950 gram H_2O and 0·4119 gram CO_2.

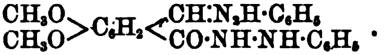
	Found.			
	I.	II.	III.	
C	68·07	67·75	67·32	per cent.
H	6·06	5·88	6·37	,,
N	14·23	14·40	—	,,

The above analyses, each of which was performed with a different preparation, agree fairly well with either of the two formulæ, $C_{38}H_{37}N_7O_5$ or $C_{22}H_{22}N_4O_3$, thus:—

	$C_{38}H_{37}N_7O_5$.	$C_{22}H_{22}N_4O_3$.
C	67·95 per cent.	67·69 per cent.
H	5·51 ,,	5·65 ,,
N	14·60 ,,	14·36 ,,

The first of these formulæ results from the combination of berberal with three molecules of phenylhydrazine with loss of two molecules of water, thus:—$C_{20}H_{17}NO_7 + 3C_6H_5{\cdot}NH{\cdot}NH_2 = C_{38}H_{37}N_7O_5 + 2H_2O$. The second formula represents the phenylhydrazide of the phenylhydrazine compound of pseudopianic acid, thus:—$C_{10}H_{10}O_5 + 2C_6H_5{\cdot}NH{\cdot}NH_2 = C_{22}H_{22}N_4O_3 + 2H_2O$.

This compound would be represented by the formula



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}CH{:}N_2H{\cdot}C_6H_5\\CO{\cdot}NH{\cdot}NH{\cdot}C_6H_5\end{matrix}.$$

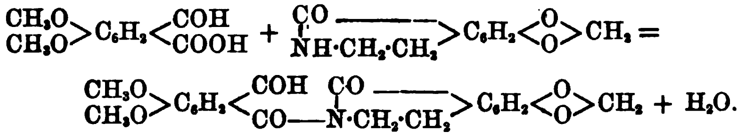
A more careful examination of the course of the reaction appears to favour the latter view. The mother liquors, aqueous as well as alcoholic, from the crude phenylhydrazine compound were mixed with a little dilute hydrochloric acid, evaporated to a small bulk, and filtered hot. The solution on standing deposited a small quantity of brownish plates, which after recrystallisation melted at

178—180°, and showed all the properties of the anhydride $C_{10}H_9NO_3$. It is, therefore, probable that in the above reaction berberal is first decomposed under the influence of water at 180° into the anhydride $C_{10}H_9NO_3$ and pseudopianic acid, and the latter then combines with two molecules of phenylhydrazine as described above. Experiments on the action of phenylhydrazine on pseudopianic acid would settle this point, but these, owing to lack of material, have not yet been instituted.

The phenylhydrazine compound $C_{22}H_{22}N_4O_3$ is very sparingly soluble in water, ethyl and methyl alcohols, benzene, chloroform, and cold amyl alcohol, but readily in hot amyl alcohol; from the latter it crystallises on cooling in small, glistening, yellow needles, which do not melt when heated to 250°. It dissolves readily in hot glacial acetic acid, but does not crystallise out again on cooling. When heated with alcoholic hydrogen chloride, the compound is readily decomposed, with formation of phenylhydrazine hydrochloride.

Synthesis of Berberal.

It has been shown in the preceding sections that berberal is readily decomposed by boiling dilute sulphuric acid into the anhydride $C_{10}H_9NO_3$ and pseudopianic acid; and it appeared extremely interesting to determine whether by bringing these two substances together under suitable conditions berberal might be reproduced, thus :—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COH\\COOH\end{matrix} + \begin{matrix}CO\text{———————}\\|\qquad\qquad\\NH{\cdot}CH_2{\cdot}CH_2\end{matrix}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2 =$$

$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}COH\quad CO\text{——————}\\ \qquad\quad |\qquad\qquad\\CO\text{——}N{\cdot}CH_2{\cdot}CH_2\end{matrix}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2 + H_2O.$$

After numerous fruitless experiments, this synthesis was ultimately accomplished by simply heating the two substances together :— 0·4 gram of $C_{10}H_9NO_3$ and 0·5 gram of pseudopianic acid were very finely powdered, intimately mixed, and heated in a test-tube gradually to 180°, kept at that temperature for 15 minutes, and then heated at 210° for 15 minutes. During the operation a quantity of water was given off, and the strongly fluorescent, brownish, oily residue solidified to a transparent resin, which cracked all over. This was ground up, dissolved in boiling alcohol, and the solution concentrated and allowed to stand for 24 hours. The sandy, crystalline precipitate which separated was collected, washed with a little alcohol, and twice recrystallised from that solvent. In this way, beautiful glistening plates, were obtained, which melted at 148—150°, and gave the following results on analysis :—

0·1558 gram substance gave 0·0652 gram H_2O and 0·3566 gram CO_2.

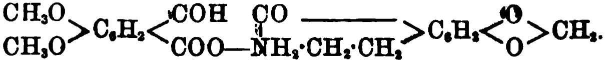
0·2310 gram substance gave 7·9 c.c. nitrogen; $t = 22°$; bar. = 745 mm.

	Theory. $C_{20}H_{17}NO_7$.	Found.
C	62·66 per cent.	62·42 per cent.
H	4·43 „	4·65 „
N	3·66 „	3·73 „

A careful comparative examination showed that this substance was identical with berberal in every respect, and as the yield obtained was over 60 per cent. of the theoretical, if pseudopianic acid could be obtained in any quantity, the above would be by far the best method for preparing berberal, especially as the resulting product is so very readily purified.

Experiments on the synthesis of pseudopianic acid and of the substance $C_{10}H_9NO_3$ are in progress; as also on the synthesis of berberine from berberal.

Pseudopianate of ω-Amidoethylpiperonylcarboxylic Anhydride,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COH\quad CO\text{———————}\\COO—NH_2\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2.$$

In order to prepare this interesting substance, 1·6 grams of ω-amidoethylpiperonylcarboxylic anhydride and 1·8 grams of pseudopianic acid were intimately mixed and dissolved in a little boiling water. The hot solution, on standing, deposited slender needles, which were collected, washed with a little water, recrystallised from this solvent, and analysed with the following result:—

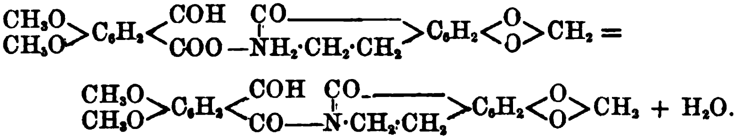
0·1304 gram substance gave 0·0601 gram H_2O and 0·2858 gram CO_2.

0·1770 gram substance gave 5·5 c.c. nitrogen; $t = 17°$; bar. = 740 mm.

	Theory. $C_{20}H_{19}NO_8$.	Found.
C	59·85 per cent.	59·77 per cent.
H	4·74 „	5·12 „
N	3·49 „	3·55 „

This substance melts at 149°, and is identical with the compound $C_{20}H_{19}NO_8$, obtained by treating berberal with alkalis as explained on p. 1075, and the formation of this substance under these conditions is evidently due to the fact that berberal on hydrolysis first yields pseudopianic acid and ω-amidoethylpiperonylcarboxylic anhydride, which on solution in water again combine, forming the compound $C_{20}H_{19}NO_8$.

When heated at 180°, the compound $C_{20}H_{19}NO_8$ loses 1 mol. H_2O and is converted into berberal. This interesting decomposition is easily understood with the aid of the equation



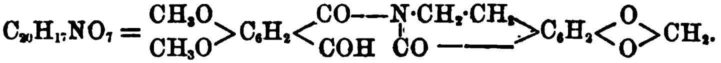
$$\begin{array}{l} \substack{CH_3O\\CH_3O}>C_6H_2<\substack{COH\\COO}\ \substack{CO\text{————————}\\-NH_2\cdot CH_2\cdot CH_2}>C_6H_2<\substack{O\\O}>CH_2 = \\ \qquad \substack{CH_3O\\CH_3O}>C_6H_2<\substack{COH\\CO}\ \substack{CO\text{——————}\\\text{——}N\cdot CH_2\cdot CH_2}>C_6H_2<\substack{O\\O}>CH_2 + H_2O. \end{array}$$

A sample of berberal obtained in this way gave the following results on analysis:—

0·0998 gram substance gave 3·2 c.c. nitrogen; t = 17°; bar. = 740 mm.

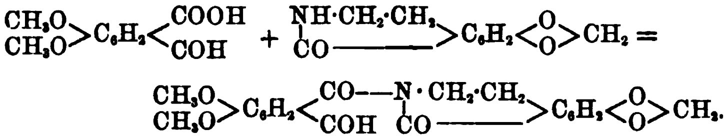
	Theory. $C_{20}H_{17}NO_7$.	Found.
N	3·66 per cent.	3·81 per cent.

Isoberberal,



$$C_{20}H_{17}NO_7 = \substack{CH_3O\\CH_3O}>C_6H_2<\substack{CO\text{——}N\cdot CH_2\cdot CH_2\\COH\ \ CO\text{————————}}>C_6H_2<\substack{O\\O}>CH_2.$$

This very interesting substance is readily prepared by heating together *opianic acid* and the anhydride $C_{10}H_9NO_3$, thus:—



$$\begin{array}{l} \substack{CH_3O\\CH_3O}>C_6H_2<\substack{COOH\\COH} + \substack{NH\cdot CH_2\cdot CH_2\\CO\text{————————}}>C_6H_2<\substack{O\\O}>CH_2 = \\ \qquad \substack{CH_3O\\CH_3O}>C_6H_2<\substack{CO\text{——}N\cdot CH_2\cdot CH_2\\COH\ \ CO\text{————————}}>C_6H_2<\substack{O\\O}>CH_2. \end{array}$$

1·6 grams of the anhydride $C_{10}H_9NO_3$ and 1·8 grams of opianic acid (prepared from narcotine by oxidation with dilute nitric acid) were ground up together and the mixture heated in a small flask, at 210—215° for thirty minutes. The reaction took place exactly as described in the synthesis of berberal (p. 1079), and the resulting brown, fluorescent oil solidified on cooling to an exactly similar, transparent resin. This was ground up and boiled with a considerable quantity of alcohol until completely dissolved, the solution concentrated, filtered, and allowed to stand for about two hours. The crystalline precipitate, which was slightly greyish and possessed a remarkable satiny lustre, was collected, washed with a little alcohol, dried on a porous plate, and recrystallised from boiling toluene. The solvent leaves undissolved a small quantity of a brownish substance, and on cooling beautiful, faintly yellow, lustrous plates are obtained, which, after drying at 100°, gave the following results on analysis :—

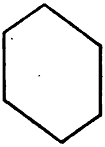
0·1490 gram substance gave 0·0629 gram H_2O and 0·3422 gram CO_2.

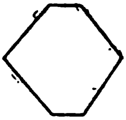
0·1986 gram substance gave 6·3 c.c. nitrogen; $t = 15°$; bar. = 740 mm.

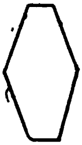
	Theory. $C_{20}H_{17}NO_7$.	Found.
C	62·66 per cent.	62·53 per cent.
H	4·43 „	4·57 „
N	3·66 „	3·76 „

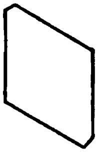
Isoberberal melts at 185° (berberal melts at 149—150°). It is very readily soluble in hot and cold glacial acetic acid, moderately in boiling xylene, toluene, or benzene, and alcohol, but only very sparingly soluble in these solvents in the cold, as also in light petroleum. The solutions fluoresce in exactly the same way as those of berberal.

Isoberberal crystallises from boiling xylene in stellate groups, from boiling toluene in flat plates. The best shaped crystals were obtained by allowing a moderately concentrated solution of the substance in hot dilute acetic acid to cool very slowly. Beautiful, colourless crystals were deposited which, when examined under the microscope, were seen to have the following forms :—





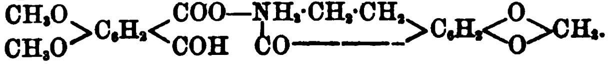




Isoberberal, like berberal, is apparently very readily hydrolysed by acids and alkalis, the products being obviously opianic acid and ω-amidoethylpiperonylcarboxylic anhydride.

The yield of isoberberal obtained by the above synthesis is good, and although only small quantities of material have so far been employed, as much as 80 per cent. of pure isoberberal has in one or two cases been obtained.

Opianate of ω-Amidoethylpiperonylcarboxylic Anhydride,



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}COO—NH_2{\cdot}CH_2{\cdot}CH_2\\COH\quad CO\text{———————}\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}O\\O\end{matrix}\!>\!CH_2.$$

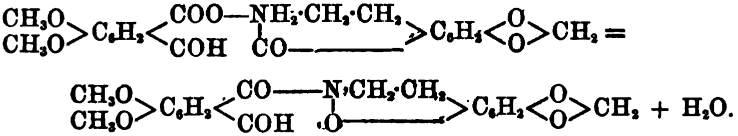
This was prepared by mixing equimolecular parts of opianic acid and ω-amidoethylpiperonylcarboxylic anhydride and dissolving the mixture in boiling water. The hot solution, on cooling, deposited the salt in the form of beautiful, feathery groups of needles, which were recrystallised from water and analysed with the following results:—

0·1544 gram substance gave 0·0688 gram H_2O and 0·3394 gram CO_2.

0·2258 gram substance gave 7·1 c.c. nitrogen; $t = 17°$; bar. = 742 mm.

	Theory. $C_{20}H_{19}NO_8$.	Found.
C	59·85 per cent.	59·95 per cent.
H	4·74 ,,	4·94 ,,
N	3·49 ,,	3·56 ,,

This substance melts at about 130—132° with decomposition. It is readily soluble in hot water, moderately in cold water, extremely soluble in alcohol, but only sparingly in bisulphide of carbon, chloroform, benzene, and light petroleum. It is isomeric with the corresponding pseudopianic salt (p. 1080), and behaves in a manner exactly similar to this salt on heating at 180°, yielding isoberberal:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}COO—NH_2\cdot CH_2\cdot CH_2\\ \quad\;\; \vert \\ COH\quad CO—————\end{matrix}\!>\!C_6H_4\!<\!\begin{matrix}O\\O\end{matrix}\!>\!CH_2 =$$

$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}CO——N\cdot CH_2\cdot CH_2\\ \qquad\quad \vert \\ COH\quad O—————\end{matrix}\!>\!C_6H_2\!<\!\begin{matrix}O\\O\end{matrix}\!>\!CH_2 + H_2O.$$

The salt was heated at 180° for about ten minutes, and the resulting oil, which solidified to a transparent resin on cooling, recrystallised from boiling toluene. The beautiful, satiny crystals which separated melted at 185° and showed all the properties of isoberberal.

Analysis:—

0·1323 gram substance gave 4·2 c.c. nitrogen; $t = 14°$; bar. = 738 mm.

	Theory. $C_{20}H_{17}NO_7$.	Found.
N	3·66 per cent.	3·74 per cent.

Separation of Oxyberberine, Dioxyberberine, and Anhydroberberilic Acid.

These three compounds occur, together with inorganic salts, in the precipitate which separates from the sulphurous acid liquors on evaporation (p. 1012).

Before proceeding to the separation of the organic compounds, the precipitate is gently warmed with 5 per cent. hydrochloric acid, until the evolution of sulphurous anhydride ceases, filtered, washed with water, and dried on a porous plate. It is then tested by heating on a platinum spatula, and the treatment with dilute hydrochloric acid repeated if more than traces of inorganic matter are left. The separation of the organic compounds is a matter of some difficulty, but may be accomplished fairly completely by either of the following methods:—

Method I.—The precipitate is boiled with glacial acetic acid, until about two-thirds of it has dissolved; the solution is filtered hot, and the yellow residue, which contains dioxyberberine, washed with a little acetic acid and purified as described on p. 1088. The dark-coloured filtrate is evaporated to half its bulk and allowed to stand in a cool place; in a short time the separation of beautiful, orange-coloured crystals of oxyberberine acetate commences, and at the end of seven days these are collected, washed with acetic acid, dried at 100°, and further purified as described on p. 1085. The dark-coloured mother liquors from these crystals, after evaporation to a small bulk, deposit a further quantity of orange-coloured crystals of oxyberberine acetate, mixed with a small quantity of silky needles of anhydroberberilic acid. These two substances may be separated with difficulty by repeated recrystallisation from glacial acetic acid, but the quantity of either ultimately obtained is but small.

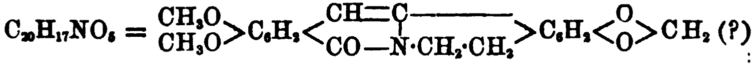
Method II.—The precipitate is dissolved in boiling dilute alcoholic potash, the solution filtered hot and rapidly cooled under the tap. The beautiful, needle-shaped crystals of oxyberberine which separate are collected, washed with alcohol, and purified as described on p. 1085. The alcoholic mother liquor from these is evaporated to about half its bulk, cooled, filtered from a further quantity of oxyberberine which separates, acidified with dilute sulphuric acid, and boiled for a few minutes to decompose any berberilic acid present. The tarry mass which separates is collected, washed with water and repeatedly triturated with hot alcohol; this treatment removes a dark-brown, resinous substance, leaving a yellow, amorphous powder which consists for the most part of dioxyberberine (p. 1087).

Method I is best employed if dioxyberberine is the principal product required, whereas method II appears to give the best yield of oxyberberine.

The relative quantities of these substances present in the crude precipitate varies with almost every preparation, but in one or two cases approximately the following amounts have been obtained from 1 kilo. of berberine hydrochloride:—

Crude yellow precipitate	25 grams.
Oxyberberine	10 „
Dioxyberberine	4 „
Anhydroberberilic acid	2 „

Oxyberberine,



$$C_{20}H_{17}NO_6 = {CH_3O \atop CH_3O}{>}C_6H_2{<}{CH{=}\overset{}{C}\text{———————} \atop CO{-}N{\cdot}CH_2{\cdot}CH_2}{>}C_6H_2{<}{O \atop O}{>}CH_2\ (?)$$

This interesting substance differs from berberine in containing 1 oxygen atom more than the alkaloïd; it may, therefore, be looked on as the primary product of the oxidation of berberine. It is best purified by recrystallisation either from xylene or from glacial acetic acid. The pure substance dried at 100° gave, on analysis, the following numbers:—

I. 0·1628 gram substance gave 0·0752 gram H_2O and 0·4088 gram CO_2.

0·2457 gram substance gave 8·9 c.c. nitrogen; $t = 25°$; bar. = 740 mm.

II. 0·1635 gram substance gave 0·0743 gram H_2O and 0·4088 gram CO_2.

III. 0·1654 gram substance gave 0·0770 gram H_2O and 0·4162 gram CO_2.

	Theory. $C_{20}H_{17}NO_6$.		Found.		
		I.	II.	III.	
C	68·39 per cent.	68·48	68·19	68·63	per cent.
H	4·84 „	5·13	5·04	5·17	„
N	3·96 „	3·93	—	—	„

This beautiful, yellow substance melts at 198—200° to a deep-yellow liquid, which may be heated to 250° without decomposition; even at 280° it is only slightly discoloured. It is moderately soluble in boiling toluene and xylene, very soluble in hot acetic acid (see below), and still more so in acetic anhydride; sparingly soluble in alcohol and benzene, almost insoluble in light petroleum and water; the alcoholic solution shows a slight blue fluorescence. It crystallises from xylene in beautiful, lustrous, yellow plates. Oxyberberine is slightly soluble in hydrochloric acid, readily so in an alcoholic solution of hydrogen chloride; the addition of alcoholic platinum chloride to this produces a yellow precipitate which appears to be amorphous, but crystallises from alcohol in slender, silky needles.

Oxyberberine is very sparingly soluble in dilute sulphuric acid (1 : 4) but dissolves readily in warm 50 per cent. sulphuric acid, and the yellow solution, on cooling, deposits beautiful, light-yellow needles. It gives the following very delicate reaction, by means of which the smallest trace of the substance may be detected. A minute particle of the substance is dissolved in a little warm 50 per cent. sulphuric acid, cooled, and one drop of ordinary concentrated nitric acid added.

A deep-brown coloration is at once produced, which rapidly changes to an intense violet; on the addition of water the colour is not destroyed, but turns a fine reddish-violet, which is very similar in appearance to the colour of a very dilute solution of permanganate.

Oxyberberine dissolves in a warm solution of hydrogen iodide, and if a trace of iodine is added, a brown precipitate is produced, which crystallises from alcoholic hydrogen iodide in green plates or groups of slender microscopic needles.

In order to determine whether oxyberberine is capable of forming an acetyl derivative, a small quantity of the substance was boiled with an excess of acetic anhydride in a reflux apparatus for four hours, evaporated to a small bulk, and allowed to stand over night. The beautiful, yellow, needle-shaped crystals which formed were collected, washed with acetic anhydride, and dried at 130°.

The analysis showed that the substance was unchanged:—

0·1548 gram substance gave 0·0712 gram H_2O and 0·3904 gram CO_2.

	Theory. $C_{20}H_{17}NO_5$.	Found.
C........	68·39 per cent.	68·78 per cent.
H........	4·84 „	5·11 „

Oxyberberine Acetate, $C_{20}H_{17}NO_5,C_2H_4O_2$.

Although oxyberberine, as compared with berberine, is a very feeble base, it forms a very well characterised acetate; this is readily obtained in a pure state by dissolving the substance in boiling glacial acetic acid, and allowing the solution to stand for some days. The acetate gradually separates in beautiful, lustrous, yellow crystals; these are collected, drained on a porous plate, and dried by exposure to the air for three days. An analysis gave the following numbers:—

0·1370 gram substance gave 0·0642 gram H_2O and 0·3238 gram CO_2.

	Theory. $C_{20}H_{17}NO_5,C_2H_4O_2$.	Found.
C........	64·23 per cent.	64·39 per cent.
H........	5·11 „	5·21 „

It is moderately stable at ordinary temperatures, if the crystals are large, but the finely-powdered substance gradually loses acetic acid on exposure to the air. A sample of the preparation analysed above was finely powdered and allowed to stand exposed to the air for four days; on analysis it gave C = 65·30 : H = 5·28, and on drying at 100° it lost only 10·9 per cent. of acetic acid.

Dried at 100°, the beautifully lustrous crystals become opaque, and rapidly lose the whole of their acetic acid, leaving a residue of pure oxyberberine. A small quantity of the acetate dried at 100° for two hours gave, on analysis, the following results:—

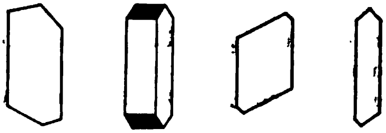
0·1474 gram substance gave 0·0660 gram H_2O and 0·3704 gram CO_2.

	Theory. $C_{20}H_{17}NO_6$.	Found.
C........	68·39 per cent.	68·53 per cent.
H........	4·84 „	4·97 „

1·8586 gram of the pure acetate, heated at 100° until the weight was constant, lost 0·2702 gram of acetic acid = 14·54 per cent.

$C_{20}H_{17}NO_6(C_2H_4O_2)$ contains 14·59 per cent. of acetic acid.

The beautiful crystals of oxyberberine acetate, when examined under the microscope, seem to have the following forms:—

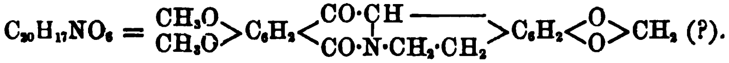


As this acetate is moderately easily soluble in glacial acetic acid, its molecular weight was carefully determined by Raoult's method, with the following result:—

Substance taken	1·5730 grams.
Acetic acid taken	100·4 „
Melting point of acetic acid	16·262°
„ „ mixture	16·112°
Depression of the melting point...	0·150°
Molecular weight of the substance found from the above data	407
Theory for $C_{20}H_{17}NO_6,C_2H_4O_2$	411

The yield of oxyberberine is about 10 grams from 1 kilo. of berberine hydrochloride, and as it can thus be obtained in considerable quantity, I hope to make it the subject of a future investigation.

Dioxyberberine,



$$C_{20}H_{17}NO_6 = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CO\cdot CH\text{————}\\ \quad | \\ CO\cdot N\cdot CH_2\cdot CH_2\end{matrix}\!>C_6H_2<\!\begin{matrix}O\\O\end{matrix}\!>CH_2\ (?).$$

This remarkable substance, which probably results from the further action of oxidising agents on oxyberberine, is unfortunately produced in such small quantity and is so difficult to purify, that it has been found impossible to investigate it as thoroughly as could have been wished.

The crude yellow product obtained as explained on p. 1012, is almost insoluble in the usual solvents, but it may be obtained pure by recrystallisation either from boiling aniline, nitrobenzene, or ethyl benzoate, the former being preferable on account of its somewhat lower boiling point. In recrystallising it, the powder is added to boiling aniline as long as it is dissolved, the solution rapidly filtered, and allowed to cool; the whole operation being conducted as quickly as possible, as boiling with aniline decomposes the substance and great loss occurs. The hot solution, on cooling, deposits the new substance in glistening, yellow needles, which are collected, washed first with aniline and then with methyl alcohol, and dried on a porous plate.

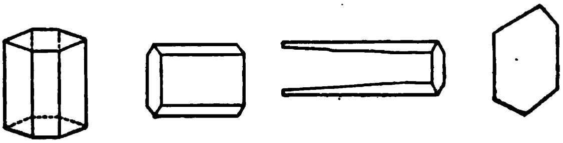
For the analysis the substance was dried at 100° for one hour :—

I. 0·1740 gram substance gave 0·0802 gram H_2O and 0·4196 gram CO_2.
0·3469 gram substance gave 11·7 c.c. nitrogen; $t = 16°$; bar. $= 766$ mm.
II. 0·1867 gram substance gave 0·0882 gram H_2O and 0·4470 gram CO_2.
III. 0·2272 gram substance gave 0·1013 gram H_2O and 0·5470 gram CO_2.

	Theory.	Found.			
	$C_{20}H_{17}NO_6$.	I.	II.	III.	
C....	65·39 per cent.	65·76	65·29	65·66	per cent.
H....	4·64 ,,	5·17	5·25	4·95	,,
N....	3·82 ,,	3·92	—	—	,,

Each of these analyses was made with a separate preparation: I was recrystallised once from aniline; II, twice from the same solvent; and III was recrystallised from ethyl benzoate.

Dioxyberberine is almost insoluble in alcohol, benzene, and light petroleum, sparingly soluble in boiling glacial acetic acid, readily in boiling aniline, nitrobenzene, or ethyl benzoate, but only sparingly in these liquids in the cold. It crystallises from ethyl benzoate in small, well-defined crystals, which, when examined under the microscope, are seen to have the following forms :—



Some of the crystals were very curiously striated: twin crystals were frequent, as also single examples with very imperfectly formed edges.

Dioxyberberine shows the following characteristic reactions:—

It dissolves in concentrated sulphuric acid, producing a reddish-violet solution; on warming, the colour gradually changes and ultimately becomes intensely olive-green.

It dissolves in nitric acid with a fine violet colour. If a drop of nitric acid is added to its solution in cold concentrated sulphuric acid, a beautiful, deep bluish-violet coloration is produced, which is destroyed on the addition of water (compare the corresponding reaction with oxyberberine, p. 1085).

Finely-divided dioxyberberine is turned a dark green by the addition of a few drops of concentrated hydrochloric acid; on warming with an excess of hydrochloric acid, the greater part dissolves, forming a yellowish-green solution, which, on addition of a drop of platinum chloride, gradually becomes intensely violet-coloured.

Action of Alkalis on Dioxyberberine.

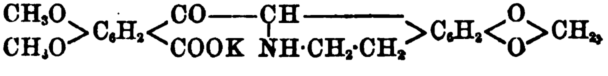
Although only sparingly soluble in aqueous solutions of alkalis, dioxyberberine dissolves with great readiness in warm alcoholic potash, forming a deep orange-red solution, which, if sufficiently concentrated, deposits on cooling, beautiful, deep orange-coloured needles of a potassium salt. In order, if possible, to obtain this in a state pure enough for analysis, pure dioxyberberine was dissolved in a strong solution of pure potassium hydrate in 80 per cent. methyl alcohol, the solution allowed to stand, and the crystals which separated quickly collected, washed with a little methyl alcohol, spread on a porous plate, and transferred to a vacuum desiccator.

Two separate preparations gave the following results on analysis:—

1. 0·2179 gram substance gave, after decomposition with sulphuric acid, 0·0404 gram K_2SO_4 = 8·31 per cent. of K.
2. 0·3371 gram substance gave 0·0698 gram K_2SO_4 = 8·09 per cent. K.

Theory for $C_{20}H_{18}NO_7K$ .... 9·22 per cent. K.
„ „ $C_{20}H_{18}NO_7K + 3H_2O$ .. 8·17 „ K.

Unfortunately, owing to the small amount of material at my disposal, it was not possible to make any further analyses of this interesting salt, but it seems probable that when dioxyberberine dissolves in alcoholic potash it forms a potassium salt of the formula



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}{>}C_6H_2{<}\begin{matrix}CO\text{——}CH\text{———}\\COOK\ \ NH\cdot CH_2\cdot CH_2\end{matrix}{>}C_6H_2{<}\begin{matrix}O\\O\end{matrix}{>}CH_2,$$

which crystallises from 80 per cent. methyl alcohol with 3 mols. of water of crystallisation. This potassium salt is partially decomposed by much water, with separation of a small quantity of a yellowish-white substance. Acids decompose the salt with separation of a light ochre-coloured precipitate, which consists of pure dioxyberberine. In order to be certain of this, the precipitate was collected, washed with water and methyl alcohol, dried on a porous plate at 100°, and analysed with the following results:—

0·1595 gram substance gave 0·0685 gram H_2O and 0·3830 gram CO_2.

	Theory. $C_{20}H_{17}NO_6$.	Found.
C........	65·39 per cent.	65·48 per cent.
H........	4·63 ,,	4·77 ,,

Hydroxylamine has no action on a dilute solution of the potassium salt. In order to prove this, 0·75 gram of pure dioxyberberine was dissolved in a considerable excess of dilute methyl alcoholic potash, 1 gram of hydroxylamine hydrochloride, dissolved in a little water, added, and the solution, after standing for 24 hours, heated to boiling for half-an-hour. The bulk of the methyl alcohol was distilled off, the residue acidified with hydrochloric acid, and the precipitate which separated washed well, and analysed with the following result:—

0·2163 gram substance gave 6·8 c.c. nitrogen; $t = 21°$; bar. = 746 mm.

	Theory. $C_{20}H_{17}NO_6$.	Found.
N........	3·82 per cent.	3·70 per cent.

The substance was therefore unchanged dioxyberberine.

The most remarkable property of the potassium salt of dioxyberberine is that, on standing in the air, it gradually loses its colour, and is converted into the potassium salt of berberilic acid. In studying this decomposition, 2 grams of pure dioxyberberine was converted into the potassium salt by dissolving it in methyl alcoholic potash, and the product, which consisted of red crystals suspended in a yellow solution, was agitated with air in a large flask for about a week, the whole being gently warmed from time to time. The solution gradually became colourless, and the red crystals ultimately entirely disappeared, giving place to a small quantity of a white, crystalline precipitate. The product was dissolved in water, neutralised with dilute hydrochloric acid, evaporated until free from alcohol, and acidified. The white, semi-solid precipitate of berberilic acid which separated was collected, washed with water, and converted into anhydroberberilic acid by boiling with 50 per cent. sulphuric acid for a few minutes. The white, crystalline precipitate thus obtained was recrystallised from much alcohol, dried at 100°, and analysed with the following result:—

0·1392 gram substance gave 0·0564 gram H_2O and 0·3070 gram CO_2.

0·1560 gram substance gave 4·8 c.c. nitrogen; $t = 21°$; bar. = 756 mm.

	Theory. $C_{20}H_{17}NO_8$.	Found.
C........	60·15 per cent.	60·15 per cent.
H........	4·26 „	4·48 „
N........	3·51 „	3·49 „

This substance melts at 237° and is identical with anhydroberberilic acid.

The formation of berberilic acid from the potassium salt of dioxyberberine may be explained by the following equation:—

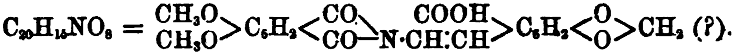
$$C_{20}H_{16}NO_7K + KOH + O_2 = C_{20}H_{17}NO_9K_2 + H_2O,$$

but it is extremely difficult to understand the *modus operandi* of the reaction. In order, however, to prove that oxygen was actually taken up in this reaction, 0·22 gram of dioxyberberine was dissolved in methyl alcoholic potash and placed in a eudiometer in an atmosphere of oxygen over mercury. After remaining for five days, with constant agitation and gentle application of heat from time to time, it was found that 11 c.c. of oxygen had been absorbed. A blank experiment was then carried out with methyl alcoholic potash solution alone, under exactly similar conditions, and, although slight absorption did take place, the diminution in the volume of oxygen after six days was only 3·2 c.c.

This experiment seems to prove that the transformation of dioxyberberine into berberilic acid in alkaline solution is due to the absorption of oxygen from the air.

Further experiments which are in progress will, it is hoped, throw light on this extremely interesting decomposition.

Berilic Acid,



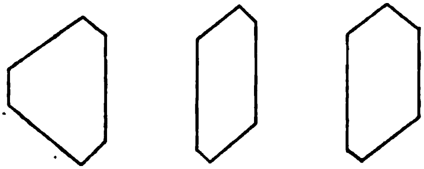
$$C_{20}H_{15}NO_8 = \begin{matrix}CH_3O\\CH_3O\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}CO\diagdown\\CO-\end{matrix}\!\!\begin{matrix}\;COOH\\N\cdot CH{:}CH\end{matrix}\!\!>C_6H_2<\!\!\begin{matrix}O\\O\end{matrix}\!\!>CH_2\ (?).$$

The crude residue, obtained as explained on p. 1012 was collected from several operations; it weighed about 6 grams, and formed a semi-solid, dark-greyish mass, from which it was extremely difficult to obtain anything crystalline. It was digested with glacial acetic acid, the dark-green solution filtered, evaporated to a small bulk, and allowed to stand for about seven days in a cool place. At the end of that time a quantity of glistening plates had separated; these were collected, well washed with glacial acetic acid, and twice recrystallised from this solvent. In this way beautiful, colourless, glistening plates were obtained, which, after drying at 105°, gave the following results on analysis:—

I. 0·1437 gram substance gave 0·0555 gram H_2O and 0·3312 gram CO_2.
0·1725 gram substance gave 5·6 c.c. nitrogen; $t = 15°$; bar. = 730 mm.
II. 0·1638 gram substance gave 0·0618 gram H_2O and 0·3762 gram CO_2.
III. 0·1580 gram substance gave 0·0608 gram H_2O and 0·3633 gram CO_2.

	Theory. $C_{20}H_{15}NO_8$.	Found. I.	II.	III.	
C......	62·99 per cent.	62·85	62·64	62·71	per cent.
H......	3·94 "	4·29	4·19	4·27	"
N......	3·67 "	3·71	—	—	"

This new acid has therefore probably the composition $C_{20}H_{15}NO_8$. When heated in a capillary tube, it darkens in colour at about 195°, and melts at 198—200° with blackening and evolution of gas; in this respect, the substance differs very markedly from any of the other compounds obtained in this research. It is only sparingly soluble in water, but readily in boiling glacial acetic acid, from which it is deposited on cooling in magnificent, lustrous plates; these, when examined under the microscope, are seen to have the following forms:—



This acid dissolves readily in sulphuric and hydrochloric acids; the solution in hydrochloric acid gives with platinum chloride a yellowish-white, amorphous precipitate, which dissolves moderately easily in hot water, and crystallises out again, on cooling, in yellow needles.

Salts of Berilic Acid.

This acid dissolves readily in alkalis, and gives very characteristic salts. The *ammonium salt* was prepared by dissolving the acid in excess of ammonia, and allowing the solution to stand over sulphuric acid in a vacuum for some days.

The silver salt, $C_{20}H_{14}AgNO_8$, was obtained, by precipitating the ammonium salt with silver nitrate, as a white, curdy precipitate, somewhat soluble in water. The well-washed salt was dried at 100°, and analysed with the following result:—

0·1966 gram substance gave 0·0570 gram H_2O and 0·3446 gram CO_2.

0·1906 gram substance gave 0·0407 gram Ag.

	Theory. $C_{20}H_{14}AgNO_8$.	Found.
C........	47·61 per cent.	47·81 per cent.
H........	2·78 „	3·22 „
Ag.......	21·43 „	21·35 „

A solution of the ammonium salt shows the following behaviour with reagents:—

Calcium Chloride.—In dilute solutions, at first there is no change, but, on standing, the calcium salt separates in glistening, leafy crystals readily soluble in hot water, sparingly in cold water.

Barium Chloride.—No precipitate in moderately dilute solutions.

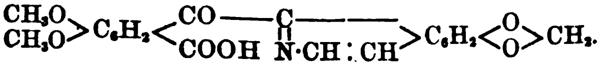
Zinc Sulphate.—Gives at once a white precipitate, consisting of tufts of needles, sparingly soluble in hot water, from which it crystallises on cooling in groups of needles and four-sided plates.

Copper Sulphate.—A light-green, amorphous precipitate, which, on warming, changes to a very light-blue, apparently crystalline precipitate, almost insoluble both in hot and cold water.

Cadmium Chloride.—A white precipitate consisting of minute tufts of needles; it dissolves in much hot water, but is more insoluble than the zinc salt.

Lead Acetate.—A white, curdy precipitate, soluble in hot water, from which it crystallises on cooling in plates, which have almost the same form as the crystals of the acid itself.

A further study of the properties of this interesting acid will, it is hoped, give more definite evidence as to its constitution, which, in the meantime, may either be represented by the formula at the head of this section or by



$$\begin{array}{l}CH_3O\\CH_3O\end{array}\!\!>C_6H_2<\!\!\begin{array}{l}CO\text{——}C\text{————}\\COOH\;\;\overset{\|}{N}\cdot CH:CH\end{array}\!\!>C_6H_2<\!\!\begin{array}{c}O\\O\end{array}\!\!>CH_2.$$

Hemipinic Anhydride, $\genfrac{}{}{0pt}{}{CH_3O}{CH_3O}>C_6H_2<\genfrac{}{}{0pt}{}{CO}{CO}>O$.

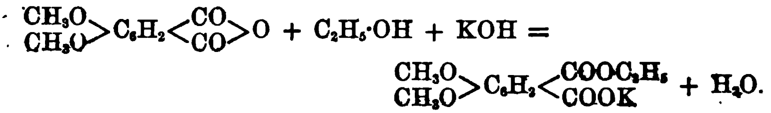
This substance, which is only produced in very small quantities in the oxidation of berberine under the conditions stated on p. 1012, was purified by repeated recrystallisation from glacial acetic acid, and thus obtained in the form of long, slightly brownish needles, which on analysis gave the following numbers:—

I. 0·1554 gram substance gave 0·0548 gram H_2O and 0·3255 gram CO_2.

II. 0·1553 gram substance gave 0·0574 gram H_2O and 0·3266 gram CO_2.

	Theory. $C_{10}H_8O_5$.	Found. I.	Found. II.	
C	57·69 per cent.	57·12	57·32	per cent.
H	3·86 „	3·91	4·10	„
O	38·54 „	38·97	38·58	„

This substance melts at 167°, and has properties very similar to those of hemipinic anhydride (m. p. 167°). On studying, however, its behaviour towards alcoholic potash, an acid melting at 146° was obtained instead of hemipinic acid (m. p. 180°), and it was not until the action of alcoholic potash on a sample of hemipinic anhydride prepared from the pure acid itself had been studied that the cause of this reaction could be explained. It was then found that hemipinic anhydride, when boiled with dilute alcoholic potash, is converted into ethyl hydrogen hemipinate:—

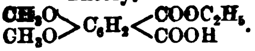


$$\genfrac{}{}{0pt}{}{CH_3O}{CH_3O}>C_6H_2<\genfrac{}{}{0pt}{}{CO}{CO}>O + C_2H_5{\cdot}OH + KOH = \genfrac{}{}{0pt}{}{CH_3O}{CH_3O}>C_6H_2<\genfrac{}{}{0pt}{}{COOC_2H_5}{COOK} + H_2O.$$

0·5 gram of the anhydride from berberine was boiled with dilute alcoholic potash for 10 minutes, mixed with twice its bulk of water, heated on a water-bath until the alcohol was expelled, cooled, and acidified with dilute hydrochloric acid. The white, crystalline precipitate formed was collected, washed with water, and recrystallised from this solvent. In this way, beautifully glistening, colourless needles were obtained, which, on drying at 100°, lost their lustre, and therefore probably contained water of crystallisation. The analysis gave the following numbers:—

I. 0·1456 gram substance gave 0·0748 gram H_2O and 0·3006 gram CO_2.

II. 0·1504 gram substance gave 0·0777 gram H_2O and 0·3115 gram CO_2.



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COOC_2H_5\\COOH\end{matrix}.$$

	Theory.	Found.	
		I.	II.
C	56·69 per cent.	56·31	56·48 per cent.
H	5·51 ,,	5·71	5·74 ,,
O	37·79 ,,	37·98	37·78 ,,

It melted sharply at 146°.

According to Anderson (*Annalen*, 86, 194), ethyl hydrogen hemipinate melts at 132·2°; Wegscheider (*Monats.*, 3, 369), on the other hand, gives 141—142° as the melting point of this salt.

In order to prove the constitution of this compound, a small quantity was dissolved in dilute sodium hydrate solution, boiled for about 10 minutes, cooled, neutralised with dilute hydrochloric acid, an excess of a strong solution of calcium chloride added, and the whole heated to boiling for a few minutes. The crystalline calcium salt which separated was collected, washed with water, and dissolved in a little hot dilute hydrochloric acid; this solution, on cooling, deposited beautiful, colourless crystals of pure hemipinic acid (m. p. 180°).

The formation of ethyl hydrogen hemipinate by the action of boiling alcoholic potash on hemipinic anhydride is very remarkable, and, in looking over the properties of a series of similar anhydrides, I have not been able to find a parallel case.

Hydrastic Acid, $C_9H_6O_6$ = $CH_2<\begin{matrix}O\\O\end{matrix}>C_6H_2<\begin{matrix}COOH\\COOH\end{matrix}$.

The crude acid solution obtained as described on p. 1013 contains two acids, namely hydrastic acid and hemipinic acid; these were separated and identified as follows:—The aqueous solution was extracted 20 times with ether, the ethereal solution dried over calcium chloride and evaporated, when a pale-yellow syrup was obtained, which, even after standing over sulphuric acid in a vacuum, showed very little sign of crystallising. As all attempts to make this syrup crystallise failed, recourse was had to the following method of purification:—The crude substance was dissolved in water, neutralised with potassium hydrate, the cold solution mixed with a large excess of a strong solution of calcium chloride, filtered, and heated to boiling. This caused the precipitation of a very sparingly soluble calcium salt, which was collected, washed with hot water, and dissolved in a sufficient quantity of boiling 5 per cent. hydrochloric acid. This solution, on cooling, deposited a quantity of brownish, leafy plates which, after repeated recrystallisation and treatment with animal charcoal, were obtained as colourless, glistening plates.

After being dried at 100°, it gave the following numbers on analysis:—

0·1540 gram substance gave 0·0455 gram H_2O and 0·2903 gram CO_2.

0·1520 gram substance gave 0·0434 gram H_2O and 0·2832 gram CO_2.

	Theory. $C_9H_6O_6$.	Found. I.	Found. II.
C	51·43 per cent.	51·41	50·81 per cent.
H	2·86 "	3·27	3·17 "
O	45·71 "	45·32	46·02 "

This acid melts at 180°, is moderately soluble in water, and crystallises from this solvent in colourless, leafy plates.

The silver salt, $C_9H_4Ag_2O_6$, was prepared by dissolving the acid in excess of ammonia, allowing the solution to stand over sulphuric acid in a vacuum until neutral, and then adding an excess of nitrate of silver solution. The white, amorphous precipitate thus produced was collected, washed with water, dried over sulphuric acid in a vacuum, and analysed with the following result:—

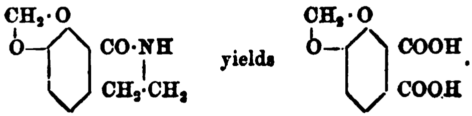
0·2009 gram substance gave 0·0230 gram H_2O and 0·1820 gram CO_2.

0·2966 gram substance gave 0·1506 gram Ag.

	Theory. $C_9H_4O_6Ag_2$.	Found.
C	25·48 per cent.	24·69 per cent.
H	0·94 "	1·27 "
Ag	50·94 "	50·78 "

This acid is therefore bibasic, and is probably identical with hydrastic acid, $C_9H_6O_6$, obtained by Freund and Lachmann (*Ber.*, **22**, 2325), which melts at 175°; as, however, no further description of the properties either of the acid itself or of its salts has as yet been published, it is impossible to speak with certainty of the identity of the two acids.

The presence of hydrastic acid among the products of the oxidation of berberine is readily understood, as this substance would result from the action of oxidising agents on ω-amidoethylpiperonylcarboxylic anhydride or one of its derivatives, thus:—



The first mother liquors from this acid were evaporated, and the syrupy residue heated in a large test-tube at 180—190° for one hour. During this operation water vapour escaped, and a small quantity of a sublimate, consisting of fine, colourless needles, formed in the cooler portions of the tube. The residue was powdered and repeatedly extracted with boiling alcohol, the alcoholic solution concentrated and allowed to stand for some hours; and the crystals which separated, collected, washed with alcohol, and repeatedly recrystallised from this solvent. In this way almost colourless needles were obtained which melted at 167°, and showed all the properties of hemipinic anhydride. It was dissolved in a little boiling alcoholic potash, and the solution diluted with water, and boiled for half an hour. The product was evaporated to a small bulk, acidified with hydrochloric acid, repeatedly extracted with ether, the ethereal solution evaporated, and the residue recrystallised from water. The crystals obtained melted at 178—180°, and showed all the properties of hemipinic acid.

Berberine Hydrogen Sulphite, $C_{20}H_{17}NO_4,H_2SO_3$.

In oxidising berberine with potassium permanganate, a small amount of the alkaloïd always escapes the action of the oxidising agent, and this, during the subsequent treatment with sulphurous acid, is converted into berberine hydrogen sulphite. This very insoluble substance is obtained in small quantity during the purification of anhydroberberilic acid (p. 1014) as a light yellow precipitate; and for a long time its constitution was a matter of doubt, as it seemed very improbable that a sulphite of berberine could be so sparingly soluble in water. It was purified by recrystallisation from very large quantities of water, dried at 100°, and analysed with the following results:—

I. 0·1734 gram substance gave 0·0749 gram H_2O and 0·3629 gram CO_2.

0·2319 gram substance gave 7 c.c. nitrogen; $t = 19°$; bar. = 748 mm.

1·4174 gram substance, boiled with dilute nitric acid until the evolution of nitrous fumes had ceased, largely diluted with water, and precipitated with barium chloride, gave 0·7750 gram $BaSO_4$.

II. 0·1188 gram substance gave 0·0504 gram H_2O and 0·2510 gram CO_2.

	Theory. $C_{20}H_{17}NO_4,H_2SO_3$.	Found. I.	Found. II.
C	57·55 per cent.	57·08	57·62 per cent.
H	4·55 „	4·80	4·71 „
N	3·36 „	3·48	— „
SO_4	23·02 „	22·71	— „

This salt is remarkably stable, and crystallises from dilute solutions of potassium carbonate unchanged. It dissolves readily in dilute nitric acid, and on cooling berberine nitrate crystallises out.

0·1712 gram substance gave 0·0740 gram H_2O and 0·3799 gram CO_2.

	Theory. $C_{20}H_{17}NO_4HNO_3$.	Found.
C	60·30 per cent.	60·40 per cent.
H	4·52 „	4·80 „

Berberine hydrogen sulphite dissolves readily in dilute hydrochloric acid, and on the addition of platinum chloride a yellow precipitate of berberine platinochloride is thrown down.

This was collected, washed with water, dried at 100°, and analysed with the following result:—

0·2284 gram substance gave 0·0718 gram H_2O and 0·3708 gram CO_2.

0·3739 gram substance gave 0·0670 gram Pt.

	Theory. $(C_{20}H_{17}NO_4)_2,H_2PtCl_6$.	Found.
C	44·47 per cent.	44·22 per cent.
H	3·33 „	3·49 „
Pt	18·02 „	17·96 „

As soon as the composition of this substance had been determined in this way, confirmatory experiments were made, with the object of preparing this salt directly from berberine; and it was found that when a solution of berberine hydrochloride is mixed with a solution of sodium hydrogen sulphite containing an excess of sulphurous acid, a precipitate is produced which has properties exactly similar to those of the salt described above. It was not thought necessary to analyse it.

Examination of the Mother Liquors of Berberilic Acid and of Berberal.

Using the methods of separation described in the preceding sections, the actual weight of crystalline substances obtained by oxidising 1 kilo. of berberine hydrochloride is only about 350—400 grams; at least half the product remains in the alcoholic mother liquors of berberilic acid and in the acetic acid mother liquors of berberal (pp. 1041, 1063, and Trans., 1889, pp. 78 and 81).

These, on evaporation, deposit thick, almost black, tarry masses, from which only small quantities of crystalline substances could be obtained by treatment with solvents. As, however, it seemed probable that very interesting compounds might be contained in these tars, the investigation of which might throw additional light on the question of the constitution of berberine, a large number of experiments were instituted with the object of decomposing these tars and thus obtaining crystalline decomposition products, the study of which would reveal the nature of the compounds actually contained in the tars. After numerous failures, the following method gave unexpectedly good results:—

The *mother liquors* of *berberilic acid* were first experimented with. These were gently heated in a dish on a water-bath until free from alcohol, and the black residue boiled briskly in a large, enamelled pan with a considerable quantity of 8—10 per cent. sulphuric acid; the whole being well stirred during the operation. After boiling for two hours, the greater portion had dissolved, forming an orange-coloured solution; this was allowed to cool, decanted from the undissolved tar, and the latter again boiled with fresh dilute sulphuric acid, the operation being continued until only a small quantity of a pitch-like substance remained, which was not further acted on by the sulphuric acid.

The resulting liquors were treated by one of the two following methods:—

Method I.—The liquors were extracted 20 times with ether; the resulting, almost colourless, flocculent ethereal solution, on standing in a cold place, deposited a quantity of crystals. These were collected, washed with ether, and recrystallised twice from water, and in this way beautiful, lustrous plates were obtained, which, after drying at 100°, gave the following numbers on analysis:—

0·1510 gram substance gave 0·0638 gram H_2O and 0·3175 gram CO_2.

0·2010 gram substance gave 6·5 c.c. nitrogen; $t = 21°$; bar. = 740 mm.

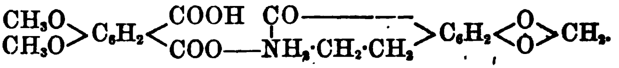
	Theory. $C_{20}H_{19}NO_9$.	Found.
C........	57·55 per cent.	57·34 per cent.
H........	4·55 „	4·69 „
N........	3·35 „	3·47 „

This substance melts at 180°, and is identical with the compound $C_{20}H_{19}NO_9$, described in Part I of this research (p. 84); it is isomeric with berberilic acid, from which it differs in the following point:—The substance dissolves readily in hot dilute sodium carbonate solution, and, on standing, lustrous crystals of the substance $C_{10}H_9NO_3$ (p. 1013) separate, and the alkaline liquors, on examination, are found to contain hemipinic acid, which can be isolated as its calcium salt in the usual way (p. 1095). A quantitative determination of the relative amounts of these decomposition products formed gave the following results:—

1·18 grams of substance yielded 0·49 gram of the anhydride $C_{10}H_9NO_3$ and 0·66 gram of calcium hemipinate. The compound $C_{20}H_{19}NO_9$ is therefore decomposed according to the equation

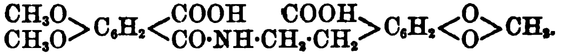
$$C_{20}H_{19}NO_9 + Na_2CO_3 = C_{10}H_9NO_3 + C_{10}H_8O_6Na_2 + CO_2.$$

according to which 1·18 grams should have yielded 0·54 gram of the substance $C_{10}H_9NO_3$ and 0·74 gram of calcium hemipinate. The substance is therefore the hydrogen hemipinic salt of $C_{10}H_9NO_3$, and has the following constitution:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COOH & CO\text{————————}\\COO\text{——} & NH_2\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2.$$

Berberilic acid, with which this substance is isomeric, has the following somewhat similar constitution:—



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}COOH & COOH\\CO\cdot NH\cdot CH_2\cdot CH_2\end{matrix}>C_6H_2<\begin{matrix}O\\O\end{matrix}>CH_2.$$

The ethereal mother liquors from this substance, on evaporation, deposited considerable quantities of a yellow, crystalline mass, which, on examination, was found to be almost pure hemipinic acid. It was purified by means of the calcium salt, recrystallised twice from water, and the beautifully colourless, lustrous prisms thus obtained were analysed with the following results:—

0·1258 gram substance gave 0·0528 gram H_2O and 0·2446 gram CO_2.

	Theory. $C_{10}H_{10}O_6$.	Found.
C	53·09 per cent.	53·02 per cent.
H	4·42 „	4·66 „
O	42·48 „	42·32 „

0·5610 gram substance, dried at 100°, lost 0·0792 gram.

$C_{10}H_{10}O_6 + 2H_2O$ contains 13·74 per cent. of water of crystallisation.
Found................ 14·11 „ „ „ „

The sulphuric acid mother liquors, from which the substance, $C_{20}H_{19}NO_9$ and hemipinic acid had been separated by extraction with ether, were mixed with just sufficient baryta-water to remove the sulphuric acid, filtered, and the yellow filtrate evaporated to a small bulk. The solution, on standing, deposited crystals, which were found to consist of a mixture of the substances $C_{10}H_{11}NO_4$ (p. 1055) and $C_{10}H_9NO_3$ (p. 1013), and in this way considerable quantities of these substances were prepared for use in subsequent work.

From these experiments, it appears that the tarry substances contained in the alcoholic mother liquors of berberilic acid still contain large quantities of this acid, which is hindered from crystallising by the presence of a small quantity of a black, tarry decomposition product.

Method II.—The acid liquors were evaporated to the crystallising point, without extracting with ether, and set aside to crystallise. After standing for seven days, the almost colourless, crystalline cake which had formed at the bottom of the dish was separated from the mother liquor, washed with a little water, and drained on a porous plate. The liquors were then carefully evaporated, allowed again to crystallise, the operation being continued as long as crystals separated. The various crops of crystals were mixed, boiled with sufficient water to completely dissolve them, the solution filtered, allowed to stand for two days, the crystals which separated collected, and recrystallised twice from water. In this way, magnificent, pale-yellow, lustrous crystals were obtained which on analysis gave the following numbers:—

I. 0·1308 gram substance gave 0·0608 gram H_2O and 0·2746 gram CO_2.

0·1910 gram substance gave 7·3 c.c. nitrogen; $t = 15°$; bar. = 750 mm.

II. 0·1450 gram substance gave 0·0648 gram H_2O and 0·3096 gram H_2O and 0·3096 gram CO_2.

0·2310 gram substance gave 9·6 c.c. nitrogen; $t = 12°$; bar. = 740 mm.

III. 0·1512 gram substance gave 0·0765 gram H_2O and 0 3201 gram CO_2.

0·2526 gram substance gave 10·0 c.c. nitrogen; $t = 20°$; bar. = 742 mm.

IV. 0·1518 gram substance gave 0·0680 gram H_2O and 0·3250 gram CO_2.

0·1338 gram substance gave 5·1 c.c. nitrogen; $t = 18°$; bar. = 750 mm.

	Theory.	Theory.	Found.			
	$C_{30}H_{30}N_2O_{13}$.	$C_{30}H_{28}N_2O_{12}$.	I.	II.	III.	IV.
C	57·51 p. c.	59·21 p. c.	57·19	58·22	57·74	58·38 p. c.
H	4·79 ,,	4·57 ,,	5·17	4·96	5·62	4·97 ,,
N	4·47 ,,	4·57 ,,	4·40	4·80	4·40	4·32 ,,

Each of these analyses was made with a different preparation.

The formula $C_{30}H_{30}N_2O_{13}$ represents the *hemipinate* of the substance $C_{10}H_9NO_3$, crystallising with one molecule of water = $(C_{10}H_9NO_3)_2C_{10}H_{10}O_6 + H_2O$; the formula $C_{30}H_{28}N_2O_{12}$ represents the anhydrous salt; it is probable that the former is the correct formula. This beautiful substance melts at about 187—189° if very quickly heated, but if slowly heated it melts at about 177° with decomposition. It is sparingly soluble in alcohol, benzene, and cold water, moderately in hot water, readily soluble in acetic acid.

The pure substance dissolves readily in hot dilute sodium carbonate solution, and on cooling, beautiful plates of the substance $C_{10}H_9NO_3$ separate out, whilst the alkaline solution contains hemipinic acid. When heated at 180—200° for a short time, decomposition sets in, a quantity of water vapour is given off, and the residue dissolved in a little boiling acetic acid deposits, on cooling, crystals of hemipinic anhydride (m. p. 167°). The substance $C_{10}H_9NO_3$ may be obtained from the mother liquors of these crystals by evaporation and recrystallising the residue from water.

The aqueous mother liquors from these yellow crystals contain considerable quantities of a second substance, which is much more readily soluble and crystallises with difficulty. The concentrated liquors on long standing deposit feathery crystals, which are difficult to obtain quite pure, owing to the fact that when recrystallised from water, they are decomposed to some extent with formation of the yellow crystals described above. A very carefully recrystallised sample of this substance gave the following results on analysis:—

0·1602 gram substance gave 0·0772 gram H_2O and 0·2964 gram CO_2.

0·2902 gram substance gave 10·7 c.c. nitrogen; $t = 20°$; bar. = 745 mm.

0·2930 gram substance, dissolved in water, acidified with hydrochloric acid, and precipitated with barium chloride, gave 0·0881 gram $BaSO_4$.

	Theory. $C_{30}H_{24}O_{14}N_2(SO_4) =$ $C_{10}H_{10}O_6(C_{10}H_{11}NO_4)_2,H_2SO_4$.	Found.
C	48·52 per cent.	50·45 per cent.
H	4·59 ,,	5·35 ,,
N	3·77 ,,	4·10 ,,
SO_4	12·94 ,,	12·35 ,,

This substance is a mixed sulphate and hemipinate of the base $C_{10}H_{11}NO_4$. It crystallises from water, in which it is readily soluble, in colourless feathery leaflets, which melt at about 190° with decomposition. The constitution of this salt is readily shown from the following experiment:—

A quantity of the substance was dissolved in warm water, just sufficient barium hydrate solution added to remove all the sulphuric acid, the product filtered, and the clear filtrate evaporated to a small bulk on a water-bath. After standing for two days, peculiar, pale-yellow, nodular crystals had formed; these were collected, washed with water, dried at 100°, and analysed with the following result:—

I. 0·1501 gram substance gave 0·0719 gram H_2O and 0·3053 gram CO_2.
0·2722 gram substance gave 9·5 c.c. nitrogen; $t = 12°$; bar. = 755 mm.

II. 0·2680 gram substance gave 9·9 c.c. nitrogen; $t = 14°$; bar. = 758 mm.

	Theory. $C_{30}H_{32}N_2O_{14} =$ $C_{10}H_{10}O_6(C_{10}H_{11}NO_4)_2$.	Found. I.	 II.	
C	55·90 per cent.	55·47	—	per cent.
H	4·97 ,,	5·32	—	,,
N	4·35 ,,	4·07	4·33	,,

The formation of this salt from the double salt just described is represented thus—

$$C_{10}H_{10}O_6(C_{10}H_{11}NO_4)_2,H_2SO_4 + Ba(OH)_2 = C_{10}H_{10}O_6(C_{10}H_{11}NO_4)_2 + BaSO_4 + 2H_2O.$$

The di-hemipinate of the base $C_{10}H_{11}NO_4$ is readily soluble in hot and moderately in cold water; it crystallises after long standing in nodular masses somewhat resembling the hydrogen hemipinate of the same base (p. 1061). It melts at about 175° with decomposition; it is moderately soluble in hot alcohol, very readily in acetic acid, and almost insoluble in benzene The strong solution in water, acidified with hydrochloric acid and mixed with platinum chloride, gives a precipitate of the platinochloride of $C_{10}H_{11}NO_4$, and on extracting the solution with ether, and evaporating the ethereal extract, a residue of hemipinic acid is obtained.

Either of the above methods may be employed for preparing considerable quantities of the substance $C_{10}H_9NO_3$ from the tarry mother liquors of berberilic acid, and both give good results, but, as a rule, method I was adopted in dealing with large quantities of these mother liquors.

Examination of the Mother Liquors of Berberal.

Before experimenting with these mother liquors, the greater bulk of the water and acetic acid was distilled off; the black, tarry residue, which obviously still contained considerable quantities of berberal, was then treated with various solvents with the view of isolating this substance, but without success. The whole of the tar was then boiled with large quantities of 20 per cent. sulphuric acid for some hours, filtered from any undissolved matter, and the reddish-brown solution allowed to stand. In the course of a few days a large quantity of bright-reddish needles had separated, these were collected, washed with water, and recrystallised from very dilute sulphuric acid; a large quantity of bright-yellow needles were obtained which were identified as sulphate of berberine.

The platinochloride prepared from this salt gave on analysis the following numbers :—

0·3271 gram substance gave 0·0587 gram platinum.

	Theory. $(C_{20}H_{17}NO_4)_2,H_2PtCl_4$.	Found.
Pt........	18·02 per cent.	17·94 per cent.

In one case, in which 1 kilo. of berberine hydrochloride had been oxidised, in the usual way, nearly 100 grams of unchanged berberine sulphate was recovered from the mother liquors of berberal by the above method.

The mother liquors from which the berberine sulphate had crystallised were concentrated, and extracted 20 times with ether; the solution on evaporation deposited a quantity of almost colourless crystals, which could not be obtained pure, but which appeared for the most part to consist of the pseudopianic salt of the substance $C_{10}H_9NO_3$ (m. p. 149°, see p. 1080). The whole quantity was dissolved in boiling sodium carbonate solution; this solution, on cooling, deposited colourless crystals of the anhydride $C_{10}H_9NO_3$, and the alkaline solution contained a considerable quantity of pseudopianic acid.

The sulphuric acid liquors which had been extracted with ether still contain a large amount of the substance $C_{10}H_9NO_3$, which may be extracted by precipitating the sulphuric acid with baryta-water and evaporating the solution. The product thus obtained is, however, very crude and difficult to purify.

These experiments seem to prove that the mother liquors of berberal and of berberilic acid do not contain any other products than those already described in this paper.

Examination of the Aqueous Mother Liquors from the Oxidation of Berberine (p. 1013).

These aqueous mother liquors, from which the bulk of the neutral organic substances had been extracted by ether, deposited, on evaporation, a quantity of a solid residue, which on examination was found to contain large quantities of organic matter.

As it was important to determine the nature of these organic substances, some qualitative experiments were first instituted. To a portion of the solution, phosphomolybdic acid was added, the precipitate which formed collected, washed, treated with alkalis, and the white, crystalline mass which separated recrystallised from water. In this way colourless plates were obtained, which after recrystallisation from water melted at 181—182°, and consisted of the anhydride $C_{10}H_9NO_3$ (p. 1013).

A second portion of the solution was acidified, extracted several times with ether, the ethereal solution evaporated, the residue neutralised, boiled with calcium chloride, and the precipitate which formed dissolved in a little hot dilute hydrochloric acid. After standing for some time, an acid separated which showed all the properties of hemipinic acid, but which seemed to be mixed with small quantities of another acid. In order to determine approximately the amount of hemipinic and other acids present in the solution, the liquors from 1 kilo. of berberine hydrochloride were neutralised, mixed with a large quantity of a saturated solution of calcium chloride, and heated to boiling for half an hour. The precipitate which formed was collected on cloth bags, well washed with hot water, and extracted with hot dilute hydrochloric acid, until no more organic matter passed into solution. The acid solution was filtered from the mass of calcium sulphate which is necessarily always present, evaporated to the crystallising point, and the dark-brown crystalline crust which separated on cooling dissolved in dilute sodium carbonate solution and boiled with freshly ignited animal charcoal for one hour. The pale-yellow filtrate was neutralised with hydrochloric acid, boiled with calcium chloride, the calcium salt which separated decomposed with hydrochloric acid, and the acid thus obtained recrystallised from water. The white, crystalline powder which was deposited from the hot solution was dried at 100°, and analysed with the following result:—

I. 0·1450 gram substance gave 0·0552 gram H_2O and 0·2808 gram CO_2.

II. 0·1550 gram substance gave 0·0550 gram H_2O and 0·3016 gram CO_2.

III. 0·1562 gram substance gave 0·0573 gram H_2O and 0·3016 gram CO_2.

	Theory. $C_{10}H_{10}O_6$.	Theory. $C_9H_6O_6$.	Found. I.	II.	III.
C....	53·10 p. c.	51·43 p. c.	52·81	53·06	52·66 p. c.
H...	4·42 ,,	2·86 ,,	4·22	3·94	4·07 ,,
O....	42·48 ,,	45·71 ,,	42·97	43·00	43·27 ,,

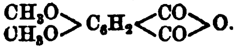
These analyses were made with different preparations.

This substance melts at 165—168° with decomposition and evolution of gas. It shows all the properties of hemipinic acid, and undoubtedly consists for the most part of this substance contaminated with a second acid (hydrastic acid?) which contains much less hydrogen.

In order to prove the presence of hemipinic acid, about 2 grams of the substance was heated at 200° for one hour, and the residue recrystallised twice from glacial acetic acid. The beautiful, colourless needles thus obtained melted at 167°, and showed all the properties of hemipinic anhydride.

Analysis:—

0·1552 gram substance gave 0·0554 gram H_2O and 0·3272 gram CO_2.



$$\begin{matrix}CH_3O\\CH_3O\end{matrix}\!>C_6H_2<\!\begin{matrix}CO\\CO\end{matrix}\!>O.$$

	Theory. $\begin{matrix}CH_3O\\CH_3O\end{matrix}>C_6H_2<\begin{matrix}CO\\CO\end{matrix}>O.$	Found.
C........	57·69 per cent.	57·49 per cent.
H........	3·84 ,,	3·96 ,
O........	38·46 ,,	38·55 ,,

INDEX OF AUTHORS' NAMES.

TRANSACTIONS. 1890.

And to such papers as appeared in the Proceedings during the Session 1889—1890 (Nos. 72—86, November, 1889, to July, 1890, inclusive), but not in the Transactions.

A.

Adie, R. H., on the sulphates of antimony, 540.

Armstrong, H. E., the oxidation of turpentine in sunlight, Proc., 1890, 99.

—— the structure of the cycloid hydrocarbons, Proc., 1890, 101.

—— the terminology of hydrolysis, especially as affected by ferments, 528.

Armstrong, H. E., and W. P. Wynne, isomeric change in the naphthalene series. No. 6. The influence of position in determining the nature of isomeric change in the case of the chloronaphthalenesulphonic acids, Proc., 1890, 86.

—— —— note on the action of potash on naphthalene-1 : 3-disulphonic acid, Proc., 1890, 136.

—— —— studies on the constitution of the tri-derivatives of naphthalene. No. 1. The constitution of β-naphthol- and β-naphthylamine-sulphonic acids R. and G. Naphthalenemetadisulphonic acid, Proc., 1890, 11.

—— —— studies on the constitution of the tri-derivatives of naphthalene. No. 2. α-Amido-1-3′-naphthalenedisulphonic acid, Proc., 1890, 15.

—— —— studies on the constitution of the tri-derivatives of naphthalene. No. 3. α-Naphthylaminedisulphonic acid Dahl No. III. The constitution of naphthol-yellow S., Proc., 1890, 16.

—— —— studies on the constitution of the tri-derivatives of naphthalene. No. 4. The constitution of α-naphthylaminedisulphonic acid Dahl No. II. Naphthalene-1 : 2′-disulphonic acid, Proc., 1890, 125.

—— —— studies on the constitution of tri-derivatives of naphthalene. No. 5. The constitution of the Schöllkopf α-naphthylaminedisulphonic acid, Proc., 1890, 126.

Armstrong, H. E., and W. P. Wynne, studies on the constitution of the tri-derivatives of naphthalene. No. 6. The constitution of Casella's β-naphthylamine-δ-disulphonic acid, Proc., 1890, 127.

—— —— studies on the constitution of the tri-derivatives of naphthalene. No. 7. The disulphonic acids obtained by sulphonating the isomeric heteronucleal β-naphthylaminesulphonic acids, Proc., 1890, 128.

—— —— studies on the constitution of the tri-derivatives of naphthalene. No. 8. β-Chloronaphthalenedisulphonic acids, Proc., 1890, 131.

—— —— the chlorides of naphthalene and its derivatives, and the manner in which they are decomposed by alkalis, Proc., 1890, 85.

—— —— the comparative influence exerted by the radicles Cl, OH, and NH_2 in naphthalene-derivatives on the formation of sulphonic acids, Proc., 1890, 133.

—— —— the homonucleal trichloronaphthalenes, Proc., 1890, 76.

—— —— the ten isomeric dichloronaphthalenes, and the sulphonic acids and trichloronaphthalenes derived therefrom, Proc., 1890, 77.

B.

Bailey, G. H., and W. B. Hopkins, the behaviour of the more stable oxides at high temperatures [Part I]. Cupric oxide, 269.

Bassett, H., the interaction of iodine, water, and potassium chlorate, 760.

Beck, C. R. See W. A. Tilden.
Bevan, E. J. See C. F. Cross.
Blackman, F. F. See S. Ruhemann.
Brown, H. T., and G. H. Morris, researches on the germination of some of the Gramineæ, Part I, 458.
—— —— note on the identity of cerebrose and galactose, 57.

C.

Campbell, J. M. See G. G. Henderson.
Carnelley, T., and W. Frew, the relative antiseptic powers of isomeric organic compounds, 636.
Chevreul, M. E., obituary notice of, 445.
Cohen, J. B. See R. Ormandy.
Collie, N., and S. B. Schryver, the action of heat on the chlorides and hydroxides of mixed quaternary ammonium compounds, 767.
Cross, C. F., and E. J. Bevan, contributions to cellulose chemistry. Acetylation of cellulose, 1.
—— —— the constituents of flax, 196.
—— —— the interaction of hypochlorites and ammonium salts. Ammonium hypochlorite, Proc., 1890, 22.
Cundall, J. T., note on the production of ozone by flames, Proc., 1890, 26.

D.

Dale, J., obituary notice of, 446.
De La Rue, Warren, obituary notice of, 441.
Dixon, A. E., note on a phenylic salt of phenylthiocarbamic acid, 268.
—— semithiocarbazides, 257.
Dobbin, L., tertiary butyl mercaptan, 639.
Duncan, C. C., the production of pure metallic copper in a crystalline condition, Proc., 1890, 95.
Dunstan, W. R., and T. S. Dymond, an investigation of the conditions under which hydrogen peroxide is formed from ether, 574, 988.
Dymond, T. S. See W. R. Dunstan.

E.

Elliott, W. J. See S. Ruhemann.

F.

Fowler, G. J., and J. Grant, the influence of different oxides on the decomposition of potassium chlorate, 272.
Frew, W. See Carnelley.

G.

Geuther, A., obituary notice of, 448.
Grant, J. See G. J. Fowler.

H.

Henderson, G. G., and J. M. Campbell, the action of chromium oxychloride on nitrobenzene, 253.
Heycock, C. T., and F. H. Neville, on the molecular weights of metals when in solution, 376, 656.
Hopkins, W. B. See G. H. Bailey.
Hughes, F. See R. Meldola.
Hutchinson, A., note on the reduction of aromatic amides, 957.

J.

Japp, F. R., and F. Klingemann, $\alpha\beta$-dibenzoylcinnamene and the constitution of Zinin's lepiden and its derivatives, 662.
—— —— reduction of α-diketones, Proc., 1890, 31.
Japp, F. R., and J. Raschen, note on a compound from benzoïn and acetone, 783.
Japp, F. R., and A. E. Turner, compounds of phenanthraquinone with metallic salts, 4.
Japp, F. R., and G. H. Wadsworth, paradesylphenol, 965.
Joule, J. P., obituary notice of, 449.
Judd, J. W., the evidence afforded by petrographical research of the occurrence of chemical change under great pressure, 404.

K.

Kipping, F. S., action of phosphoric anhydride on fatty acids, 532, 980.
Kipping, F. S., and J. E. Mackenzie, $\alpha\alpha'$ - dimethyl - $\alpha\alpha'$ - diacetylpentane, Proc., 1890, 116.
Kipping, F. S., and W. H. Perkin, jun., action of dehydrating agents on

$\alpha\omega$-diacetylpentane. Synthesis of methylethylhexamethylene, 13.

Kipping, F. S., and W. H. Perkin, jun., action of reducing agents on $\alpha\omega$-diacetylpentane. Formation of dimethylheptamethylene, Proc., **1889**, 145.

—— —— derivatives of phenylhexamethylene, 304.

—— —— $\alpha\omega$-diacetyl-$\alpha\omega$-diethylpentane, 29.

Klingemann, F. See F. R. Japp.

L.

Langer, C. See L. Mond.

Lewkowitsch, J., Benedikt's acetyl-values, Proc., **1890**, 72, 91.

Linder, S. E., and H. Picton, note on the hydrosulphides, Proc., **1890**, 49.

Ling, A. R., halogen derivatives of quinone, Proc., **1890**, 33.

Lloyd, F. J., milk of abnormal quality, 201.

M.

Mackenzie, J. E. See F. S. Kipping.

Marsh, J. E., a new monobromocamphor, 828.

Marsh, J. E., and R. Stockdale, the production of camphor from turpentine, 961.

Marshall, T. R., and W. H. Perkin, jun., acetyltrimethylenecarboxylic acid, Proc., **1890**, 137.

—— —— $\omega\omega_1$-diacetylbutane, 241.

Meldola, R., the formation of triazine derivatives, 328.

Meldola, R., and F. Hughes, a third naphthaquinone, 631.

—— —— note on the action of nitric acid on dibrom-α-naphthol, 808.

—— —— the formation of indene-derivatives from dibrom-α-naphthol, 893.

Meldola, R., and F. W. Streatfeild, researches on normal and mixed diazoamides, 785.

Mond, L., C. Langer, and F. Quincke, action of carbon monoxide on nickel, 749.

Montgomery, J. W., obituary notice of, 453.

Moody, G. T., and T. G. Nicholson, paraxylenesulphonic acids, 974.

Morris, H. G. See H. T. Brown.

N.

Neville, F. H. See C. T. Heycock.

Nicholson, T. G. See G. T. Moody.

Nickels, B., obituary notice of, 452.

North, B. See T. E. Thorpe.

O.

Ormandy, R., and J. B. Cohen, a new method for the estimation of nitrates and nitrites in waters, 811.

O'Sullivan, C., arabinon, the saccharon of arabinose, 59.

O'Sullivan, C., and F. W. Tompson, invertase: a contribution to the history of an unorganised ferment, 834.

P.

Page, D., obituary notice of, 453.

Pappel, A., and H. D. Richmond, the milk of the gamoose, 754.

Pedler, A., note on the explosion of sulphuretted hydrogen and of the vapour of carbon bisulphide with air and oxygen, 625.

—— the action of chlorine on water in the light, and the action of light on certain chlorine acids, 613.

—— the action of light on phosphorus and some of the properties of amorphous phosphorus, 599.

Perkin, W. H., jun., ethyl $\alpha\alpha_1$-diacetyladipate, 204.

—— note on the preparation of pyrocatechol, 587.

—— on berberine, Part II, 992.

Perkin, W. H., jun., and A. Schloesser, diphenylfufuran, 944.

Perkin, W. H., jun., and J. B. Tingle, acetylcarbinol (acetol), Proc., **1889**, 156.

Perkin, W. H., jun. See also F. S. Kipping and T. R. Marshall.

Pickering, S. U., note on the law of the freezing points of solutions, Proc., **1890**, 9.

—— the nature of solutions, as elucidated by a study of the density, electric conductivity, heat capacity, heat of dissolution, and expansion by heat of sulphuric acid solutions, 64.

—— the nature of solutions as elucidated by the freezing point of sulphuric acid solutions, 331.

Picton, H. See S. E. Linder.

Pullinger, F., action of zinc on dilute sulphuric acid, 815.

Q.

Quincke, F. See L. **Mond.**

R.

Ramsay, W., nitrogen trioxide and peroxide, 590.
Raschen, J. See F. R. **Japp.**
Richardson, A., action of light on moist oxygen, PROC., 1889, 134.
Richmond, H. D. See A. **Pappel.**
Robinson, H. H. See T. E. **Thorpe.**
Romanis, R., obituary notice of, 455.
Ronalds, E., obituary notice of, 456.
Ruhemann, S., action of chloroform and alcoholic potash on hydrazines, 50.
—— contributions to the knowledge of mucic acid. Part III. Hydromuconic acid, 370.
Ruhemann, S., and F. F. **Blackmann**, contributions to the knowledge of mucic acid. Part I. Hydromuconic acid, 370.
Ruhemann, S., and W. J. **Elliott**, contributions to the knowledge of mucic acid. Part II. Action of phosphoric chloride on mucic acid, 931.

S.

Schloesser, A. See W. H. **Perkin**, jun.
Schryver, S. B. See N. **Collie.**
Shenstone, W. A., some improved vacuum joints and taps, 958.
Smith, A., on desylacetophenone, 643.
Stockdale, R. See J. E. **Marsh.**
Streatfeild, F. W. See R. **Meldola.**

T.

Thorpe, T. E., and B. **North**, diethylphosphorous acid, 634.
Thorpe, T. E., and H. H. **Robinson**, frangulin, 38.
Thorpe, T. E., and A. E. **Tutton**, phosphorous oxide. Part I, 545.
Thresh, J. C., a new method of estimating the oxygen dissolved in water, 185.
Tilden, W. A., and C. R. **Beck**, some crystallised substances obtained from the fruits of various species of *Citrus*, 323.
Tingle, J. B., action of ethyl oxalate on camphor, 652.
Tingle, J. B. See also W. H. **Perkin**, jun.
Tompson, F. W. See C. **O'Sullivan.**
Turner, A. E. See F. R. **Japp.**
Tutton, A. E., crystallographical relations of the derivatives of dibenzoylcinnamene, 714.
Tutton, A. E. See also T. E. **Thorpe.**

V.

Vernon, H. M., the action of hydrochloric acid on manganese dioxide: manganese tetrachloride, PROC., 1890, 58.

W.

Wadsworth, G. H., action of aldehydes and ammonia on α-diketones, 8.
Wadsworth, G. H. See also F. R. **Japp.**
Waldie, D., obituary notice of, 456.
Werner, E. A., contributions to the chemistry of the thiocarbamides: interaction of benzyl chloride and allyl bromide respectively, with thiocarbamide, monophenylthiocarbamide, and diphenylthiocarbamide, 283.
Wynne, W. P. See H. E. **Armstrong.**

INDEX OF SUBJECTS.

TRANSACTIONS. 1890.

And to such papers as appeared in the Proceedings during the Session 1889—1890 (Nos. 72—86, November, 1889, to July, 1890, inclusive), but not in the Transactions.

A.

Acetol, Proc., 1889, 156.
Acetone and benzoïn, compound from, 783.
Acetonebenzil, preparation of, 673.
Acetovaleric acid, 230.
Acetyl-ω-amidoethylpiperonylcarboxylic anhydride, 1016.
Acetylanhydroberberilic acid, 1041.
Acetylcarbinol, Proc., 1889, 157.
Acetyl-αω-diethylcaproic acid, ω-, 36.
—— —— oxime, ω-, 37.
Acetylparadesylphenol, 968.
Acetylphenanthraquinol, Proc., 1890, 31.
Acetylpseudocumylhydrazine, 55.
Acetyltrimethylenecarboxylic acid, Proc., 1890, 137.
Acetyl-values, Benedikt's, Proc., 1890, 72, 91.
Acids, fatty, acetyl-values of, Proc., 1890, 72, 91.
—— —— action of phosphoric anhydride on, 532, 980.
Adipic acid, dibrom-, 371.
—— —— dichlor-, 939.
Alcohol, influence of, on the action of invertase on cane-sugar, 860.
Alkalis, influence of, on the action of invertase on cane-sugar, 852.
Alkyldiazoamides, 785.
—— mixed, general remarks on the nature of the combination between, 798.
Alloys, behaviour of, near their freezing points, 387.
—— eutectic, of tin, 386.
Allyl imidophenylthiocarbamate, 302.
—— phenylimidophenylthiocarbamate, 303.
Allylphenylsemithiocarbazide, 262.
Allyltriphenylpyrrholone, 707.
—— crystallography of, 743.
Alumina, influence of, on the decomposition of potassium chlorate, 276.
Aluminium, effect of, on the freezing point of tin, 385.
Amides, aromatic, reduction of, 957.
Ammonium hypochlorite, Proc., 1890, 22.
—— salts and hypochlorites, interaction of, Proc., 1890, 22.
Ammonium-compounds, mixed quaternary, action of heat on the chlorides and hydroxides of, 767.
Amylo-hydrolyst, 531.
Anhydroberberilamide, 1046.
Anhydroberberilanilide, 1047.
Anhydroberberilic acid, 994, 1037.
—— —— constitution of, 998.
—— —— salts of, 1037.
—— —— synthesis of, 1061.
—— chloride, 1042.
Anilido-3-diphenyl-5-phenylpyrrholone, [1-], 683.
Anisamide, reduction of, 957.
Annual general meeting, March 27th, 1890, 426.
Anthracene formula, Proc., 1890, 102.
Antimony, effect of, on the freezing point of tin, 387.
—— oxide, influence of, on the decomposition of potassium chlorate, 275, 277.
—— sulphates of, 540.
Antiseptic powers of isomeric organic compounds, 636.
Arabinon, 59.
Arsenic oxide, influence of, on the decomposition of potassium chlorate, 277.

B.

Balance Sheet of the Chemical Society from March 18, 1889, till March 20, 1890, 438.
—— —— of the Research Fund from March 18, 1889, till March 20, 1890, 439.
Barium oxides, influence of, on the decomposition of potassium chlorate, 280.
Barley, culture of excised embryos of, on nutrient solutions, 483.
—— culture of excised embryos of, on water, 482.
—— malted, distribution of diastase in, 508.
—— structure of a grain of, 461.
Benzaldehyde and ammonia, action of, on diacetyl, 8.
Benzene, nitro-, action of chromium oxychloride on, 253.
Benzeneazo-β-naphthylamine, triazine from, 329.
Benzene-formula, Proc., 1890, 101.
Benzile, reduction of, Proc., 1890, 31.
Benzobutyl alcohol, 309.
—— —— oxime, 310.
Benzoïn and acetone, compound from, 783.
Benzyl imidophenylthiocarbamate, 296.
—— phenylimidophenylthiocarbamate, 298.
—— thiocarbamate, preparation, reactions, and properties of, 293.
Benzylidenepseudocumylhydrazine, 55.
Berberal, 1062.
—— action of alkalis on, 1075.
—— action of phenylhydrazine on, 1077.
—— constitution of, 1002.
—— examination of, 1000.
—— hydrolysis of, 1064.
—— synthesis of, 1079.
Berberilic acid, 994, 1048.
—— —— action of heat on, 1051.
—— —— constitution of, 998.
—— —— hydrolysis of, 1053.
—— —— salts of, 1049.
Berberine, 992.
—— constitution of, 1003.
—— hydrogen sulphite, 1096.
—— oxidation of, with potassium permanganate, 1010.
Berberoline, constitution of, 1009.
Berilic acid, 1091.
—— —— salts of, 1092.
Bismuth, effect of, on the freezing point of tin, 384.
Bis-1-phenyl-3-methyl-4-methylene-5-pyrazolone, 222.
Borneol, preparation of, from terpene, 963.
Butyl mercaptan, tertiary, 639.

C.

Cadmium, effect of, on the freezing point of tin, 383.
Calcium, effect of, on the freezing point of tin, 384.
—— oxide, influence of, on the decomposition of potassium chlorate, 280.
Camphene, constitution of, 964.
Camphor, a new monobromo-, 828.
—— action of ethyl oxalate on, 652.
—— constitution of, 832, 964.
—— isobromo-, 828.
—— production of, from turpentine, 961.
Camphor-oxalic acid, 653.
—— —— reduction of, 654.
Camphorsulphonic acid, bromo-, 833.
Carbon bisulphide, explosion of, with air or oxygen, 625.
Catechol, preparation of, 587.
Cellulose, acetylation of, 1.
—— constitution of, 3.
—— existence of an enzyme which dissolves, in the seeds of grasses, 497.
—— flax, characters of, 199.
—— pentacetate, 2.
Cerebrose and galactose, identity of, 57.
Ceryl alcohol from flax, 198.
Chemical change under great pressure, evidence of, afforded by petrographical research, 404.
Chloric acid, action of light on, 624.
Chlorine, action of, on water in the light, 613.
Chromium oxide, influence of, on the decomposition of potassium chlorate, 277.
Cinnamaldehyde and ammonia, action of, on diacetyl and on phenanthraquinone, 11.
Cinnamenyldimethyglyoxaline, 11.
Cinnamenyldiphenyleneoxazole, 12.
Citrus, crystalline substances obtained from the fruits of various species of, 323.
Cobalt sesquioxide, influence of, on the decomposition of potassium chlorate, 278.
Conductivity, electrical, of sulphuric acid solutions, 86—88, 158—160.
Copper, effect of, on the freezing point of tin, 379.
—— hydrosulphide, Proc., 1890, 50.
—— oxide, behaviour of at high temperatures, 269.

Copper oxide, influence of, on the decomposition of potassium chlorate, 279.
—— pure, production of, in a crystalline condition, Proc., **1890**, 95.
Cryohydrates, nature of, 361.
Crystallography of dibenzoylcinnamene-derivatives, 714.
Cupric. See Copper.

D.

Densities of sulphuric acid solutions, 69—85, 139—158.
Desylacetophenone, 643.
—— action of phenylhydrazine on, 647.
—— oximes of 650.
Desylanisoïl, para-, 969.
Desylphenol, para-, 965.
—— —— fusion of, with caustic potash, 971.
—— —— reduction of, with hydriodic acid, 971.
Diacetyl, action of, benzaldehyde and ammonia on, 8.
—— action of cinnamaldehyde and ammonia on, 11.
—— action of salicylaldehyde and ammonia on, 10.
$\omega\omega_1$-Diacetylbutane, 241.
Diacetyl-αω-diethylpentane, αω-, 29, 32.
—— dioxime, 33.
Diacetylparadesylphenol, 968.
Diacetylpentane, αω-, action of dehydrating agents on, 13.
—— —— action of reducing agents on, Proc., **1889**, 145.
—— —— condensation products of, 26.
Diastase, distribution of, in malted barley, 508.
—— does the aleurone-layer secrete ?, 520.
—— genesis and distribution of the two varieties of, in the resting and germinating seed, 505.
—— localisation of the secretion of, in the embryo, 493.
—— of secretion, 509.
—— of secretion, action of, on ungelatinised starch, 510.
—— of translocation, 509.
Diazoamides, normal and mixed, 785.
Diazometanitrobenzene-methylparatoluidide, combination of with diazoparabromobenzene - methylparatoluidide, 793.
Diazo-β-naphthalene-methylparatoluidide, combination of, with diazoparabromobenzene - methylparatoluidide, 797.
Diazoparabromobenzene - methylparatoluidide, combination of diazometanitrobenzene - methylparatoluidide with, 793.
—— —— combination of diazo-β-naphthalene - methylparatoluidide with, 797.
Dibenzoylamidoethylpiperonylcarboxylic acid, 1059.
Dibenzoylcinnamene, αβ-, 662.
—— action of bromine on, 711.
—— action of heat on, 677.
—— action of hydroxylamine on, 710.
—— action of phenylhydrazine on, 708.
—— crystallography of, 715.
—— distillation of, 685.
—— nitro-, 676.
—— preparation of, 672.
Dibenzoylcinnamenimide, 692.
—— crystallography of, 718.
—— dibromide, 693.
Dibenzoylpentane, αω-, action of dehydrating agents on, 27.
Diethyl β-dichloromuconate, 934.
Diethylphosphorous acid, 634.
Dihexyl ketone, hydrazone of, 535.
—— —— oxime of, 535.
—— —— preparation of, 533.
Dihexylcarbinol, 536.
Dihydroxydimethylheptamethylene, ortho-, Proc., **1889**, 145.
Dihydroxynaphthalene, 633.
Diketones, α-, action of aldehydes and ammonia on, 8.
—— reduction of, Proc., **1890**, 31.
Dilaurylcarbinol, 983.
Dilaurylcarbinyl acetate, 984.
Dimethyl berberilate, 1050.
—— dipropyl glycol, Proc., **1890**, 138.
Dimethyl-ω-acetylcaproic acid, αω-, Proc., **1890**, 117.
Dimethyl - αα′ - diacetylpentane, αα′-, Proc., **1890**, 116.
Dimethyldiethylammonium chloride and hydroxide, action of heat on, 780.
Dimethylheptamethylene, formation of, Proc., **1889**, 145.
Dimethylpimelic acid, αα′-, Proc., **1890**, 117.
Dioxyberberine, 1003, 1087.
—— action of alkalis on, 1089.
—— constitution of, 1008.
Dipalmitylcarbinyl acetate, 987.
Diphenyl-β-benzoylpropionic acid, α-, 681.
—— —— action of heat on, 685.
—— —— action of hydroxylamine on, 683.
—— —— action of phenylhydrazine on, 682.

Diphenyl-β-benzoylpropionic acid, ethylamide of, 706.
—— —— methylamide of, 703.
—— —— reduction of, 681.
Diphenylfurfuran, 944, 953.
—— reduction of, 955.
—— tetrabromo-, 954.
Diphenylfurfurancarboxylic acid, 951.
—— —— action of bromine on, 953.
Diphenylfurfurandicarboxylic acid, 951.
Diphenyl-αβ-naphthotriazine, 331.
Diphenyl-5-phenylpyrrholidone, [3-], 683, 696.
Diphenyltetrazine, nitro-, 51.
Diphenylthiocarbamide, action of allyl bromide on, 303.
—— action of benzyl chloride on, 297.
Dipseudocumyltetrazine, 56.
Dispersion of phosphorous oxide, 566.
Dissolution, heat of, of sulphuric acid solutions, 94—114, 165—177.
Ditolyltetrazine, dibromopara-, 51.
—— nitro-ortho-, 54.
—— nitropara-, 51.
—— ortho-, 52.
—— para-, 50.
Ditolyltetrazinesulphonic acid, ortho-, 53.

E.

Electrical conductivity of sulphuric acid solutions, 86—88, 158—160.
Embryo and endosperm, relations of, 474.
—— form in which reserve starch enters, 513.
—— localisation of the secretion of diastase in the, 493.
—— visible changes occurring in, during germination, 466.
—— young, secretion of an amylohydrolyst [diastase] by, 489.
Embryos, excised, development of, upon foreign endosperms, 478.
—— —— of barley, culture of, on nutrient solutions, 483.
—— —— —— culture of, on water, 482.
Endosperm and embryo, relation of, 474.
—— functions of the starch of, 478.
—— visible changes occurring in, during germination, 466.
Endosperms, foreign, development of excised embryos upon, 478.
Enzymes, 835.
—— hydrolytic, origin of the, of germinated grain, 511.
Ether, action of light on, 574.
Ether, action of ozone on, 584.
—— slow combustion of, 585.
Ethyl camphor-oxalate, phenylhydrazone, 655.
—— $\alpha\alpha_1$-diacetyladipate, 204, 215.
—— —— action of phenylhydrazine on, 221.
—— —— decomposition of, by heat, 224.
—— αω-diacetyl-αω-diethylpimelate, 30.
—— αω-diacetylvalerate, 228.
—— —— hydrolysis of, 229.
—— dibenzoylsuccinate, preparation of, 949.
—— dibromadipate, 372.
—— dichloradipate, 939.
—— β-dichloromuconate, 933.
—— diïmidodiethyladipate, 218.
—— αα′-dimethyl-αα′-diacetylpimelate, Proc., 1890, 117.
—— dimethylpimelate, Proc., 1890, 117.
—— diphenylhydrazinediacetyladipate, 221.
—— disodiodiacetyladipate, 216.
—— isomuconate, 374.
—— phenylacetylhexamethylenecarboxylate, 319.
—— phenylhexamethylenedicarboxylate, 315.
Ethylamidoethylpiperonylcarboxylic anhydride, 1035.
Ethylbromopiperonylcarboxylic anhydride, ω-amido-, 1017.
Ethylmethyldihydropentene methyl ketone, 251.
Ethylmethylhexamethylene, α-iodo-, 23.
Ethylorthotolylsemithiocarbazide, 262.
Ethylpiperonylcarboxylic acid, ω-amido-, action of heat on, 1058.
—— —— —— action of methyl iodide on, 1059.
—— —— —— action of nitrous acid on, 1060.
—— —— —— preparation of, 1053.
—— —— —— salts of, with acids, 1056.
—— —— ω-chlor-, 1029.
—— anhydride, ω-amido-, 993, 1013.
—— —— —— fusion of, with potash, 1015.
—— —— —— opianate of, 1082.
—— —— —— pseudopianate of, 1076, 1080.
—— —— nitrosoamido-, 1018.
Ethyltriphenylbromopyrrholone, crystallography of, 736.
Ethyltriphenylpyrrholone, 704.
—— action of bromine on, 705.
—— crystallography of, 730.

Expansion by heat of sulphuric acid solutions, 114—121, 177—184.

F.

Fats, examination of, Proc., 1890, 72, 91.
Ferments, terminology of hydrolysis, especially as affected by, 528.
—— unorganised, 835.
Ferric oxide, influence of, on the decomposition of potassium chlorate, 278.
Flames, production of ozone by, Proc., 1890, 26.
Flax, constituents of, 196.
Frangulin, 38.
—— hydrolysis of, 45.
—— preparation of, 41.
Freezing points of solutions, law of, Proc., 1890, 9.
—— —— of sulphuric acid solutions, 331.

G.

Galactose and cerebrose, identity of, 57.
Gamoose, milk of the, 754.
Geddic acid, 59.
Germination, changes in the embryo and endosperm during, 466.
—— of some of the Gramineæ, 458.
Glyceride-hydrolyst, 531.
Gold, effect of, on the freezing point of tin, 378.
Grain, germinated, origin of the hydrolytic enzymes of, 511.
Gramineæ, germination of, 458.
Grasses, existence of a cellulose-dissolving enzyme (cytohydrolyst) in the germinating seed of, 497.

H.

Heat capacity of sulphuric acid solutions, 88–94, 160–164.
—— of dissolution of sulphuric acid solutions, 94–114, 165–177.
—— of fusion of nitrogen tetroxide, 593.
Hemipinic anhydride, 1094.
Hydrastic acid, 1095.
Hydrazines, action of chloroform and potash on, 50.
Hydriodic acid, effect of, on the dissolution of zinc in dilute sulphuric acid, 824.
Hydrocarbons, cycloid, structure of, Proc., 1890, 101.
Hydrodesylphenol, 970.
Hydrogen peroxide, conditions of the formation of, from ether, 574, 988.
—— —— formation of, from moist ether, Proc., 1889, 134.
—— —— formation of, on exposure of water to light, Proc., 1889, 134.
—— —— influence of, on the dissolution of zinc in sulphuric acid, 822.
—— sulphide, explosion of, with air or oxygen, 625.
—— —— influence of, on the dissolution of zinc in sulphuric acid, 821.
Hydrolysis, terminology of, 528.
Hydrolysts, 531.
Hydrolyte, 531.
Hydromucic acid, 371, 937.
Hydrosulphides, Proc., 1890, 50.
Hydroxyadipic acid, chloro-, lactone of, 940.
Hydroxybenzamide, para-, reduction of, 957.
Hydroxyethylbromonitropiperonylcarboxylic anhydride, 1027.
Hydroxyethylbromopipeperonylcarboxylic acid, ω-, 1025.
—— anhydride, ω-, 1025.
Hydroxyethylcatecholcarboxylic anhydride, ω-, 1027.
Hydroxyethylnitropiperonylcarboxylic anhydride, ω-, 1027.
Hydroxyethylpiperonylcarboxylic acid, ω-, 996, 1020.
—— —— formation of, 1060.
—— —— fusion of, with potash, 1022.
—— —— oxidation of, 1022.
—— —— salts of, 1023.
—— anhydride, ω-, 1021.
—— —— action of phosphoric chloride on, 1029.
Hydroxyhydromuconic acid, lactone of, 942.
Hydroxyindone, brom-, 400.
—— —— benzylamide of, 403.
—— —— hydrazone and hydrazone-hydrazide of, 402.
—— —— β-naphthylamide of, 403.
Hydroxyphenyldimethylgloxaline, 10.
Hypochlorites and ammonium salts, interaction of, Proc., 1890, 22.
Hypochlorous acid, action of light on, 622.
Hyposulphurous acid, influence of, on the action of zinc on dilute sulphuric acid, 822.

I.

Indene derivatives, formation of, from dibrom-α-naphthol, 393.

Indium, effect of, on the freezing point of tin, 385.
Indone, α-brom-, action of aniline on, 398.
—— —— preparation of, 396.
Inversion by invertase, theory of, 918.
Invertan, α-, 894.
Invertan, β-, 896.
Invertan, γ-, 901.
Invertan, δ-, 903.
Invertan, ε-, 904.
Invertan, ζ-, 908.
—— absorption spectrum of, 912.
—— molecular weight of, 911.
Invertan, η-, 913.
Invertan-copper compounds, 914.
Invertan-series, constitution of, 921.
Invertase, 834, 896.
—— action of, on cane-sugar, 843.
—— effect of heat on solutions of, 899.
—— influence of foreign substances on the action of, on cane-sugar, 852.
—— preparation of, 869.
—— purification of, 884.
—— theory of inversion by, 918.
Iodic acid, preparation of, 760.
Iodine, water, and potassium chlorate, interaction of, 760.
Isoberberal, 1081.
—— constitution of, 1002.
Isodibenzoylcinnamene, 707.
Isolepiden, reduction of, 691.
Isomeric organic compounds, antiseptic powers of, 636.
Isomuconic acid, 373.
Isoxylepidenic acid, 690.

J.

Joints, vacuum, 958.

L.

Laurone, preparation of, 981.
—— oxime, 983.
Lead, effect on, on the freezing point of tin, 381.
—— peroxide, influence of, on the decomposition of potassium chlorate, 279.
Lemon oil, crystalline deposit from, 327.
Lepiden, Zinin's, constitution of, 662.
Light, action of chlorine on water in, 613.
—— action of, on chloric acid, 624.
—— action of, on ether, 574.
—— action of, on ether, in presence of oxygen and water, 574, 988.
Light, action of, on hypochlorous acid, 622.
—— action of, on moist oxygen, PROC., 1889, 134.
—— action of, on phosphorus, 599.
Limettin, 323.

M.

Magnesium, effect of, on the freezing point of tin, 381.
Magnetic rotation of phosphorous oxide, 567.
Manganese dioxide, action of hydrochloric acid on, PROC., 1890, 58.
—— —— influence of, on the decomposition of potassium chlorate, 277.
—— tetrachloride, PROC., 1890, 58.
Mercuric oxide, influence of, on the decomposition of potassium chlorate, 279.
Mercury, effect of, on the freezing point of tin, 383.
—— hydrosulphide, PROC., 1890, 51.
Metals, molecular weight of, when in solution, 376, 656.
Metamorphism produced by pressure, 410.
Methyl anhydroberberilate, 1039.
—— ω-chlorethylpiperonylcarboxylate, 1032.
Methyldehydropentone, PROC., 1890, 138.
Methyldehydropentonecarboxylic acid, PROC., 1890, 138.
Methyldihydropentene methyl ketone, 232, 242.
—— —— —— oxime, 236.
—— —— —— pinacone of, 248.
Methyldihydropentenedicarboxylic acid, 233.
—— —— action of bromine on, 234.
—— —— action of hydrobromic acid on, 235.
Methyl-3-diphenyl-5-phenylpyrrholidone, [1-,], 701.
Methyl-3-diphenyl-5-phenylpyrrholone, [1-], 698.
Methylethylhexamethylene, ortho-, 25.
—— synthesis of, 13.
Methylethylpentamethylene, 250.
Methylhexamethylenemethylcarbinol, 21.
Methylhexamethylenemethylcarbinyl acetate, 22.
Methyl-α-iodoethylpentamethylene, 249
Methylpentamethylenemethylcarbinol, 245.
Methylpentamethylenemethylcarbinyl acetate, 249.

Methylpentamethylenemethylcarbinyl iodide, 249.
Methylphenylsemithiocarbazide, 261.
Methyltetrahydrobenzene methyl ketone, ortho-, 16.
—— —— —— hydrazone, 20.
—— —— —— oxime, 18.
Methyltetrahydrobenzenemethylcarbinol, 24.
Methyltriphenylbromopyrrholone, crystallography of, 728.
Methyltriphenylpyrrholone, action of bromine on, 699.
—— crystallography of, 724.
—— oxidation of, 701.
Milk, abnormal, 201.
—— of the gamoose, 754.
Molecular weight of ζ-invertan, 911.
—— —— of nitrogen trioxide, 595.
—— —— of phosphorous oxide, 551.
—— weights, determination of, by Raoult's method, 804.
—— —— of metals when in solution, 376, 656.
Mucic acid, 931, 937.
—— —— action of phosphorus pentachloride on, 931.
—— —— derivatives of, 370.
Muconamic acid, β-dichloro-, 934.
Muconamide, β-dichloro-, 935.
Muconic acid, 375.
—— —— β-dichloro-, 932.
—— —— —— action of reducing agents on, 936.

N.

Naphthalene chlorides, Proc., 1890, 85.
—— —— action of alkalis on, Proc., 1890, 85.
—— constitution of the tri-derivatives of, Proc., 1890, 11, 15, 16, 125, 126, 127, 128, 131.
Naphthalene-derivatives, comparative influence exerted by the radicles Cl, OH, and NH_2 in, on the formation of sulphonic acids, Proc., 1890, 133.
Naphthalene - 1 : 2′ - disulphonic acid, Proc., 1890, 125.
Naphthalene - 1 : 3 - disulphonic acid, action of potash on, Proc., 1890, 136.
Naphthalenedisulphonic acid, α-amido-1 : 3′-, Proc., 1890, 15.
—— acids, β-chloro-, Proc., 1890, 131.
Naphthalene-formula, Proc., 1890, 102.
Naphthalenes, dichloro-, the ten isomeric, and the sulphonic acids, and the trichloronaphthalenes derived therefrom, Proc., 1890, 77.
Naphthalenes, trichloro-, homonucleal, Proc., 1890, 76.
Naphthalene-series, isomeric change in the, Proc., 1890, 86.
Naphthalenesulphonic acids, chloro-, influence of position in determining the nature of the isomeric change in, Proc., 1890, 86.
Naphthalenetrisulphonic acid, Proc., 1890, 125.
Naphthaquinone, a third, 631.
Naphthol, dibrom-α-, action of nitric acid on, 808.
—— —— preparation of, 395.
Naphtholsulphonic acids, β-, constitution of, Proc., 1890, 11.
Naphthol-yellow, S., constitution of, Proc., 1890, 16.
Naphthylaminedisulphonic acid, α-, Dahl No. II, constitution of, Proc., 1890, 125.
Naphthylaminedisulphonic acid, α-, Dahl No. III, constitution of, Proc., 1890, 16.
Naphthylaminedisulphonic acid, the Schöllkopf α-, constitution of, Proc., 1890, 126.
Naphthylamine - δ - disulphonic acid, Casella's β-, constitution of, Proc., 1890, 127.
Naphthylaminesulphonic acids, isomeric heteronucleal β-, the disulphonic acids obtained by sulphonating the, Proc., 1890, 128.
Naphthylaminesulphonic acids, β-, constitution of, Proc., 1890, 11.
Nickel, action of carbon monoxide on, 749.
—— carbon oxide, 750.
—— effect of, on the freezing point of tin, 378.
—— sesquioxide, influence of, on the decomposition of potassium chlorate, 278.
Nitrates and nitrites in water, estimation of, 811.
Nitric acid, effect of, on the dissolution of zinc by dilute sulphuric acid, 824.
Nitrites and nitrates in water, estimation of, 811.
Nitrogen peroxide, 590.
—— tetroxide, physical properties of, 591.
—— —— preparation of, 590.
—— trioxide, 590.
—— —— molecular weight of, 595.
—— —— preparation of, 591.
—— —— properties of, 597.

O.

Octohydrodiphenylfurfuran, 955.
Opianic oxime, 1070.
Organic compounds, isomeric, antiseptic powers of, 636.
Oxides, influence of, on the decomposition of potassium chlorate, 272.
—— more stable, behaviour of, at high temperatures, 269.
Oxyberberine, 1003, 1085.
—— acetate, 1086.
—— constitution of, 1008.
Oxygen dissolved in water, estimation of, 185.
—— moist, action of light on, Proc., **1889**, 134.
Oxyhydrastinine, synthesis of, from methyl chlorethylpiperonylcarboxylate, 997, 1034.
Oxylepiden, acicular, distillation of, 688.
Oxylepidenic acid, crystallography of, 747.
Ozone, action of, on ether, 584.
—— production of, by flames, Proc., **1890**, 26.

P.

Palladium, effect of, on the freezing point of tin, 380.
Palmitone oxime, 986.
—— preparation of, 985.
Petrographical research, evidence afforded by, of chemical change under great pressure, 404.
Phenanthraquinone, action of cinnamaldehyde and ammonia on, 11.
—— compounds of, with metallic salts, 4.
—— mercuric chloride, 6.
—— mercuric cyanide, 7.
—— reduction of, Proc., **1890**, 31.
—— zinc chloride, 5.
Phenanthrone, Proc., **1890**, 31.
Phenyl phenylthiocarbamate, 268.
Phenylamidoethylpiperonylcarboxylic anhydride, 1036.
Phenyldehydrohexonecarboxylic acid, 308.
Phenyldimethylglyoxaline, 9.
Phenylhexamethylene, derivatives of, 304.
—— methyl ketone, 320.
—— —— —— oxime, 321.
Phenylhexamethylenecarboxylic acid, 316, 322.
Phenylhexamethylenedicarboxylic acid, 315.
Phenylorthotolylsemithiocarbazide, 259.
Phenylpentamethylene bromide, ω-, 313.
—— glycol, ω-, 311.
Phenylthiocarbamide, action of allyl bromide on, 301.
—— action of benzyl chloride on, 295.
Phosphorous oxide, 545.
—— —— action of chlorine on, 572.
—— —— action of heat on, 552.
—— —— action of light on, 552.
—— —— action of oxygen on, 569.
—— —— action of ozone on, 571.
—— —— action of water on, 567.
—— —— crystallography of, 554.
—— —— dispersion of, 566.
—— —— magnetic rotation of, 567.
—— —— molecular weight of, 551.
—— —— physiological action of, 573.
—— —— preparation of, 547.
—— —— refraction equivalent of, 564.
—— —— relative density of, 557.
—— —— specific volume of, 558.
—— —— thermal expansion of, 560.
Phosphorus, action of light on, 599.
—— amorphous, properties of, 599.
—— odour of, 573.
—— specific volume of, 562.
Physiological action of phosphorous oxide, 573.
Pinene, constitution of, 964.
Potassium chlorate, influence of different oxides on the decomposition of, 272.
—— —— iodine, and water, interaction of, 760.
—— dichromate, influence of, on the decomposition of potassium chlorate, 280.
—— nitrate, influence of, on the decomposition of potassium chlorate, 282.
—— permanganate, influence of, on the decomposition of potassium chlorate, 280.
Pressure, effect of, on chemical action, 408.
Propyltriphenylpyrrholone, crystallography of, 738.
Proteïd-hydrolyst, 531.
Pseudocumylhydrazine, 54.
Pseudocumylhydrazinepyruvic acid, 55.
Pseudocumylsemicarbazide, 55.
Pseudomeconine, formation of, from pseudopianic acid, 1072.
Pseudomeconinic acid, 1073.
—— —— salts of, 1074.
Pseudopianic acid, action of potassium hydroxide on, 1067.
—— —— constitution of, 1001.
—— —— preparation of, 1064.
—— —— reactions of, 1066.
—— —— reduction of, 1072.

Pseudopianic acid, salts of, 1067.
—— oxime, 1069.
—— —— action of heat on, 1070.
Pyrene formula, Proc., 1890, 103.
Pyrocatechol, preparation of, 587.

Q.

Quinone, halogen derivatives of, Proc., 1890, 32.
—— isomeric change in the halogen derivatives of, Proc., 1890. 32.
—— nitro-, Étard's, probable non-existence of, 255.

R.

Raoult's method, determination of molecular weights by, 804.
Refraction equivalent of phosphorous oxide, 564.
Rhamnus frangula, frangulin from, 38.

S.

Salicylaldehyde and ammonia, action of, on diacetyl, 10.
Salicylamide, reduction of. 957.
Seed, resting and germinating, genesis and distribution of the two varieties of diastase in the, 505.
Semithiocarbazides, 257.
—— relations between the solubilities and melting points of, 264.
Silica, influence of, on the decomposition of potassium chlorate, 276.
Silver, effect of, on the freezing point of tin, 377.
—— oxide, influence of, on the decomposition of potassium chlorate, 279.
Sobrerol, Proc., 1890, 100.
Sobrerone, Proc., 1890. 100.
Sodium dibromoparaxylenesulphonate, 978.
—— effect of, on the freezing point of tin, 380.
—— paraxylenesulphonate, 978.
Solution, molecular weight of metals in, 376, 656.
Solutions, law of the freezing points of, Proc., 1890, 9.
—— nature of, 65.
—— nature of, as elucidated by the freezing points of sulphuric acid solutions, 331.
Specific volume of phosphorus, 562.
Spectrum, absorption-, of ζ-invertan, 912.
Starch, growth of excised embryos on, 489.
—— in the endosperm, functions of, 478.
—— reserve, changes of, in the growing embryo, 513.
—— —— form in which, after transformation, enters the embryo, 513.
—— ungelatinised, action of diastase of secretion on, 510.
Stearone oxime, 539.
—— preparation of, 537.
Sugar, cane-, action of invertase on, 843.
Sulphuric acid, action of, on antimonious oxide, 541.
—— —— dilute, action of zinc on, 815.
—— —— hydrates of, 128.
—— —— influence of, on the action of invertase on cane-sugar, 855.
—— —— monohydrate of, 130.
—— —— solutions, 64.
—— —— —— densities of, 69—86, 139—158.
—— —— —— electrical conductivity of, 86—88, 158—160.
—— —— —— expansion by heat of, 114—121, 177—184.
—— —— —— freezing points of, 331.
—— —— —— heat capacity of, 88–94, 160–164.
—— —— —— heat of dissolution of, 94–114, 165–177.
—— —— tetrahydrate of, 339.
—— anhydride, action of, on antimonious oxide, 541.
Sulphurous anhydride, action of, on the dissolution of zinc in sulphuric acid, 821.

T.

Taps, vacuum, 958.
Tetrahydroberberine, constitution of, 1005.
Tetraphenyldihydro-oiazone, 647.
—— action of excess of phenylhydrazine on, 649.
Tetraphenyldihydro-orthodiazine, 647.
—— action of excess of phenylhydrazine on, 649.
Tetraphenylenefurfuran, Proc., 1890, 32.
Tetraphenylpyrroline, ααβ-N-, 646.
Tetraphenyluvinone, 956.
Thallium, effect of, on the freezing point of tin, 379.
Thermal expansion of phosphorous oxide, 560.
Thermometer, platinum, 657.

Thermometers, mercurial, determination of fixed points on, 656.
Thiocarbamide, action of allyl bromide on, 299.
—— action of benzyl chloride on, 284.
Thiocarbamides, chemistry of, 283.
Thrombogenic enzymes, 531.
Thrombogens, 531.
Tin, eutectic alloys of, 386.
—— oxide, influence of, on the decomposition of potassium chlorate, 276.
Toluylamide, ortho-, reduction of, 957.
Tolylphenylsemithiocarbazide, ortho-, 258.
Translocation, diastase of, 509.
Triazine derivatives, synthesis of, 328.
Triethylbenzylammonium chloride and hydroxide, action of heat on, 781.
Triethylmethylammonium chloride and hydroxide, action of heat on, 779.
Trimethylallylammonium chloride and hydroxide, action of heat on, 776.
Trimethylbenzylammonium chloride and hydroxide, action of heat on, 778.
Trimethylene bromide, action of, on ethyl sodethylacetoacetate, 30.
Trimethylethylammonium chloride, action of heat on, 768,
—— hydroxide, action of heat on, 770.
Trimethylisoamylammonium chloride and hydroxide, action of heat on, 774.
Trimethylisobutylammonium chloride and hydroxide, action of heat on, 773.
Trimethylisopropylammonium chloride and hydroxide, action of heat on, 772.
Trimethylphenylammonium chloride and hydroxide, action of heat on, 777.
Trimethylpropylammonium chloride and hydroxide, action of heat on, 771.
Triphenylbutyrolactone, 680.
Triphenylchlorofurfuran, reduction of, 674.
Triphenylcrotolactone, 678.
—— action of bromine on, 678.
—— action of potash on, 680.
—— crystallography of, 716.
—— oxidation of, 679.
—— reduction of, 679.
Triphenylfurfuran, 645.
—— oxidation of, 675.
—— reduction of, 675.
—— tribromo-, 713.
Triphenyl-γ-hydroxybutyric acid, 680.
Triphenylpyrazole, 710.
Triphenylpyrroline, 645.
Triphenylpyrrolone, 694.
—— crystallography of, 720.
—— reduction of, 695.
Triphenylthiophen, 647.
Tungsten oxide, influence of, on the decomposition of potassium chlorate, 276.
Turpentine, oxidation of, in sunlight, Proc., 1890, 99.
—— production of camphor from, 961.

U.

Uranium oxide, influence of, on the decomposition of potassium chlorate, 276.

V.

Vacuum joints and taps, improved, 958.
Vanadic anhydride, influence of, on the decomposition of potassium chlorate, 276.
Volume, specific, of phosphorus, 562.

W.

Water, action of chlorine on, in the light, 613.
—— estimation of dissolved oxygen in, 185.
—— estimation of the nitrates and nitrites in, 811.

X.

Xylene, dibromopara-, preparation and properties of, 974.
Xylenesulphonamide, dibromopara-, 977.
—— —— reduction of, 979.
Xylenesulphonic acid, dibromopara-, 976.
—— acids, para-, 974.
—— chloride, dibromopara-, 977.

Y.

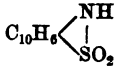
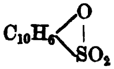
Yeast, liquefaction of, 869.
Yeast-albuminoïd, 886, 893.
Yeast-liquor, composition of, 878.

Z.

Zinc, action of, on dilute sulphuric acid, 815.
—— effect of, on the freezing point of tin, 382.
—— purification of, 816.

ERRATA.

Vol. LVII.

Page	Line			
90	18	from	top,	*for* "homopyrocatechuic" *read* "homopyrocatechol."
164	23 and 22	„	bottom,	„ "$\left.\begin{matrix}2{\cdot}0831\\3{\cdot}4925\end{matrix}\right\}2{\cdot}7878$" *read* "$\left.\begin{matrix}0{\cdot}20831\\0{\cdot}34925\end{matrix}\right\}0{\cdot}27878$."
268	4	„	„	„ "the present communication" *read* "the present and preceding communications."
551	4	„	„	„ "20·698" *read* "21·374."
„	3	„	„	„ "3·16 per cent. solution" *read* "solution containing 3·16 grams of phosphorous oxide per 100 grams of benzene."
670	bottom			*after* "pyrrol." *insert* [Editor.]
761	22	from	top,	*for* "*Annalen*" *read* "*Annales de Chimie.*"
809	bottom (note)			„ " $C_{10}H_6{<}\begin{array}{l}NH\\ \vert\\ SO_2\end{array}$" *read* " $C_{10}H_6{<}\begin{array}{l}O\\ \vert\\ SO_2\end{array}$."

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